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STUDY TO OPTIMIZE GELLANT POLYMER-WATER SYSTEMS FOR THE CONTROL OF HYPERGOLIC SPILLS AND FIRES

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16. Abstract

A system of buffered gelled water was developed to prevent and control fires from small spills of nitrogen tetroxide-(N_2O_4)-Aerozine 50-hypergolic fuel. Laboratory studies on various alkalis, buffers and seavengers for the fuel components are described. Chilling, and sodium acetate-acetic acid buffer was found to be best additive to the gelled water. Field tests are described and a delivery system (airborne) for the extinguishant is given. A short movie showing field testing is available upon request.

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FOREWORD

This report was prepared by Dow Chemical U.S.A. under NASA Contract No. NAS2-6532. The contract was administered by the Chemical Research Project Office of the National Aeronautics and Space Administration at Ames Research Center. The technical monitor for the project was Dr. G. M. Fohlen.

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I. PREFACE TO THE REPORT

By

R. R. Jennings

The safety procedures employed during capsule fueling and the emergency measures designed for use in the event of an aborted mission prevent the release of large quantities of hypergolic propellant components under any but very exceptional conditions. However, a limited but significant hazard is still presented by the accidental emission of small quantities of the propellants from a broken hose line, leakage of an unjettisoned "heel" from a fuel tank as a result of a hard landing, and so forth. These hazards can be most effectively dealt with under emergency conditions by using a special extinguishing system to isolate and deactivate the spilled hypergolic fluids.

Water containing a particulate gelling agent has been widely employed in fighting ordinary fires because it can form a "layer of water" on the fuel. It was proposed that gelled water would be more effective than ordinary water in dealing with hypergolic spills and fires, since it would immobilize and blanket the spilled fluids. However, discussions with members of the Chemical Research Projects Office of NASA's Ames Research Center indicated that a simple gelled water system would not be optimally effective against the highly reactive propellants. While the possible advantages of a gelled system were recognized, it seemed evident from their past experience with the hypergolic fluids that a satisfactory system was unlikely to be developed without the addition of chemicals capable of deactivating and detoxifying the hypergolic fluids. Accordingly, the work statement on which the contract was based called for the development of a gelled extinguishant containing chemical additives for deactivating and detoxifying both the Aerozine-50 fuel and the N_2O_4 oxidizer. In addition, the work to be performed included the design of appropriate mixing and application hardware and the elaboration of techniques for using the gelled extinguishant on spills and fires.

The contract required, as an initial step toward an optimal system, the preparation of a planning document, in which detailed consideration was to be given to the various variables involved in fire control and other hazards associated with hypergolic fluid spills. With the aid of the Technical Monitor, specific chemical agents and formulations were selected for study. The Planning Document appears as Appendix B of Part II of this report. A preliminary reading of this plan is necessary for an adequate understanding of the reasoning behind much of the reported work.

A coordinated laboratory and field testing program to optimize the gelled extinguishant system was set up in accordance with the contract work statement. The specific items for study were those selected in the planning study. The strategy was to define, insofar as possible, the composition of the gelled extinguishant in the laboratory. Further definition of the extinguishant was to take place in the field testing program, which was also designed to develop equipment and tactics.

The field program included the following tasks: (1) Determination of conditions for a credible spill situation; (2) scaling studies to assure applicability of results over a range of spill sizes; (3) exploration of suitable application equipment and tactics; (4) testing of promising formulations developed in the laboratory program; and (5) demonstration of the completed system. During the execution of the program, frequent consultations were held with the Technical Monitor to assure, insofar as possible, that the test situations would be realistic and that the procedures developed would be suitable for use in real emergencies.

It might be noted in reading the report that the chemical deactivation of the hydrazine component of the propellant system received more attention than the N_2O_4 oxidizer, although the N_2O_4 is both toxic and corrosive. This is because the Aerozine-50 presents an extra hazard since it burns readily in air and is easily ignited by a random spark or by contact with small amounts of liquid or gaseous N_2O_4. Moreover, the Aerozine-50 is also highly toxic. The work plan thus called for a laboratory search for chemical agents capable of reacting with the Aerozine-50 constituents and the Planning Document considers such agents in considerable detail. The definition of chemical groups capable of reacting with hydrazine and UDMH is also regarded as valuable in that such groups may be incorporated in fabrications designed to be pre-deployed in critical locations to catch and deactivate propellant spills.

The gelling agent used throughout this study was a commercially available fire fighting agent "GELGARD® M", which is made from a partially hydrolyzed, crosslinked acrylamide polymer. The behavior of an aqueous solution gelled with this material is affected not only by the concentration of the gelling agent, but also by the presence of other dissolved materials, both organic and inorganic. As a result of this behavior, the contract called for devising techniques to measure the consistency of various gelled formulations, since good control of consistency is required to prepare gelled extinguishant formulations for actual use. Since the flow behavior of the gelled system through a conduit is not related directly to the thickness of a layer of gelled material which can be applied to a spill, two different tests were required: one to indicate the performance of the gelled system in flow through pipes and hoses, the other to provide an index related to the ability of the formulation to form a thick layer for blanketing the spilled propellant. These tests are described in Part II of this report.

It was convenient to organize this report as four more or less independent sections even though the laboratory and field studies were coordinated in execution. The prototype system design and recommendations form the final section of the report. An important supplement to the report is the motion pictures made of the field operations. These have been assembled in an organized form for convenient reference. Examination of at least some of these films is helpful in understanding the techniques used in conducting the studies.

II. LABORATORY STUDIES

By

D. C. MacWilliams

SUMMARY

The GELGARD® M polyacrylamide combined with an aqueous acetate-acetic acid buffer to form a "pH Trap" shows good activity as a suppressant for nitrogen tetroxide and to a lesser extent, Aerozine-50. Interfacial boiling of nitrogen tetroxide was a major problem which was solved by selecting a scavenger having a low enthalpy of reaction with nitrogen tetroxide and by cooling the gel. Formaldehyde and 2,4-pentanedione were selected from a screening program and studied in detail as scavenging agents for the fuel components. These materials are of doubtful utility for the immediate suppression of the fire as compared to the neutralization of the fuel component by the acetic acid of the buffer system because of relatively slow rates of reaction. However, they do form derivatives with the fuel components which may be less toxic.

LIST OF SYMBOLS AND ABBREVIATIONS

a - Concentration of scavenger at time zero (M).

b - Concentration of fuel component at time zero (M).

c - Concentration of fuel component in all forms at time t for any given stoichiometry (M).

d - Initial concentration of acetic acid (M).

e - Initial concentration of sodium acetate (M).

k - A rate constant.

t - Time (seconds or minutes).

x - Concentration of product at time t (M).

A^- - Concentration of the conjugate base of the acid HA (M).

B - Concentration of any base (M).

BH^+ - Concentration of the conjugate acid of the base B.

E - Activation energy kcal/g mole or cal/g mole.

ΔH - Enthalpy.

ΔH° - Enthalpy in standard state (298.2°C, pure liquid or 1M solution).

H_4N_2 - Hydrazine.

HA - Concentration of any acid (M).

K - A constant which satisfies the equation $\frac{k_1}{k_2} = \exp Kx$.

HCHO - Formaldehyde.

M - Molar concentration (g moles/liter of solution).

N_2O_4 - Nitrogen tetroxide.

2,4-PD - 2,4-Pentanedione (acetylacetone).

R - Gas constant (1.986 cal/deg/g mole).

T - Any temperature (°C or °K).

T_o - Initial temperature.

ΔT - Temperature difference.

UDMH - unsym-Dimethylhydrazine.

INTRODUCTION

A detailed plan for the execution of the laboratory study of aqueous systems containing additives for control of fuel and oxidizer components and a gelling agent are given in the planning document dated July 2, 1971 (1), Appendix B. The program consisted of three distinct phases. First, selection of an alternate gellant to the polymer of choice was to be considered but not studied if the polymer of choice was satisfactory. Second, methods for the evaluation of the gels prepared using a lightly crosslinked, partially hydrolyzed polyacrylamide designated GELGARD® M were to be developed. Scavenging agents for nitrogen tetroxide incorporated in the gel were to be evaluated. Third, organic scavenging agents for the hydrazine and unsym-dimethylhydrzine (UDMH) were to be screened by thermochemical methods. The two best candidates were to be evaluated in greater detail to establish the rates of reaction. The effect of the gelling agent on the scavenging reaction was to be determined. Each of these objectives is treated as a separate topic in this report.

Two significant modifications of the work plan were made, with the concurrence of the monitor, as a result of unexpected findings in the nitrogen tetroxide absorption studies. The first was to broaden the temperature range of the studies of nitrogen tetroxide absorption from 25-50°C to 0-50°C. The second was to abandon strong bases as scavenger systems for nitrogen tetroxide in favor of the "pH Trap."

The "pH Trap" was discussed in the Planning Report (loc. cit. p. 24) as an alternate scavenger system should problems be encountered in the strong base systems for nitrogen tetroxide or in locating scavengers for the fuel components. The "pH Trap" is a buffer system which controls the pH such that the oxidizer exists in the solution as nitrite and nitrate ions and the fuel components as their conjugate acids. Table 1 shows the negative logarithms of the dissociation constants (pK_a) for various components of the fuel-oxidizer system and potential buffer pairs. The combined weight of acid and salt forms required to supply a buffer capacity of 1 g. mole toward acid or base is shown for the buffer pairs. The relative degree of neutralization of a weak acid (HA) or a weak base (B) of a given pK_a at any given pH is given by the expressions for pH/pK_a. The data for the fuels and oxidizer show that at a pH of 5.5 in aqueous solution all components are $99^+\%$ in the salt forms. Common buffer systems which will operate in this range include acetic acid-sodium acetate, monosodium succinate, and disodium citrate. The citrate system comes closest to the optimum pH of 5.5 but suffers on an equivalent weight basis when compared to acetic acid-sodium acetate. The very low solubility of succinic acid was a fatal defect. The acetic acid-sodium acetate system is soluble to about 4M but the disodium citrate crystallizes out at about 2M when ice cold. The studies concentrated on the acetic acid-sodium acetate system primarily because of the equivalent weight advantage.

TABLE 1

DISSOCIATION CONSTANTS OF OXIDIZER, FUEL AND BUFFER COMPONENTS - THE 'pH TRAP'

Acid		pK_a	
HNO_3		Strong	
HNO_2		3.4 ⟵ 5.5	
$H_5N_2^+$		8.26	
$H_3N_2Me_2^+$		7.56	
			Gram for 1 liter of 1M 1:1 Buffer
Acetic		4.75	141.10
Succinic	(1)	4.16	140.09
	(2)	5.61	
Citric	(2)	4.74	236.12
	(3)	5.40	

$$\frac{pH}{pK_a} = \log \frac{(A^-)}{(HA)} = \log \frac{B}{(BH^+)}$$

Part A: CHEMICAL IDENTITY OF THE GELLING AGENT

The laboratory studies have been made with the standard product of The Dow Chemical Company distributed under the trademark GELGARD® M. Since the laboratory work has shown that this agent may be blended with the chosen constituents for nitrogen tetroxide (N_2O_4) and Aerozine-50, deactivation studies of other gelling agents were not undertaken.

Part B: SCAVENGERS FOR NITROGEN TETROXIDE

a. EXPERIMENTAL

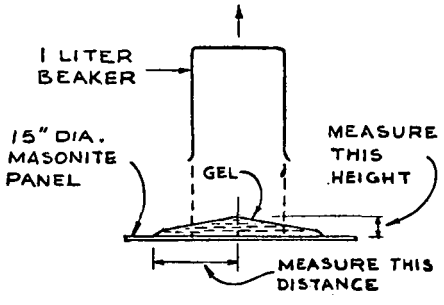
1. Angle of Repose and Flowability

The final form of the apparatus for the slump test is shown in Figure 1. A circular panel of exterior grade Masonite, 15" in diameter and 1/4" thick was supported on a wood block 8x8x3/4" in a dish pan. One liter of gel was dumped in the center of the panel and allowed to spread. After one minute and five minute intervals the radius of the heap of gel and the maximum height of the heap of gel were measured with a thin steel or plastic ruler. The ratio of the height to the radius, which is the tangent of the angle of repose, was calculated and is reported.

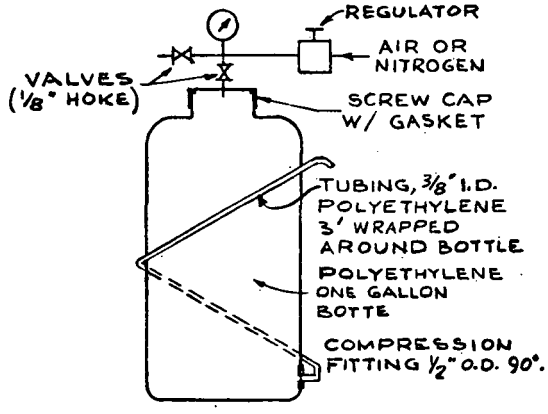
The gel flow was measured with the apparatus shown in Figure 1. A one gallon polyethylene bottle was equipped with a 1/2" outlet and a 3' length of 3/8" polyethylene tubing. A system of 1/4" valves, a pressure gage, and a regulator were attached to the screw top which was fitted with a neoprene gasket for a better seal. Compressed gas (air or nitrogen) was supplied to the regulator.

GELGARD® M polymer solutions made up in water or in dilute solutions of salt in water were known to have non-Newtonian flow properties. The effect of pressure and the length of the tube through which the gel was discharged were examined. The results are shown by a plot of the flowability index (sec/liter) vs. pressure (psi) (see Figure 2). The non-Newtonian character of the flow is evident in the curvature of the lines on the flow rate vs. pressure plot. The three-foot tube presents the same resistance to flow per foot of length as the seven foot tube at a given flow rate (e.g. 10 ml/sec.) indicating that the end effects are insignificant at least down to a ratio of tube length to diameter of 96. Flowability improves rapidly with increasing diameter of the outlet tube. For example, 50' of 1-1/2" hose with a 6' length of 1" pipe

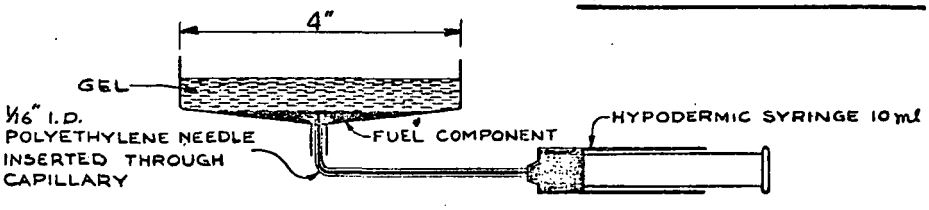
GEL TESTING



SLUMP TEST



FLOWABILITY TEST

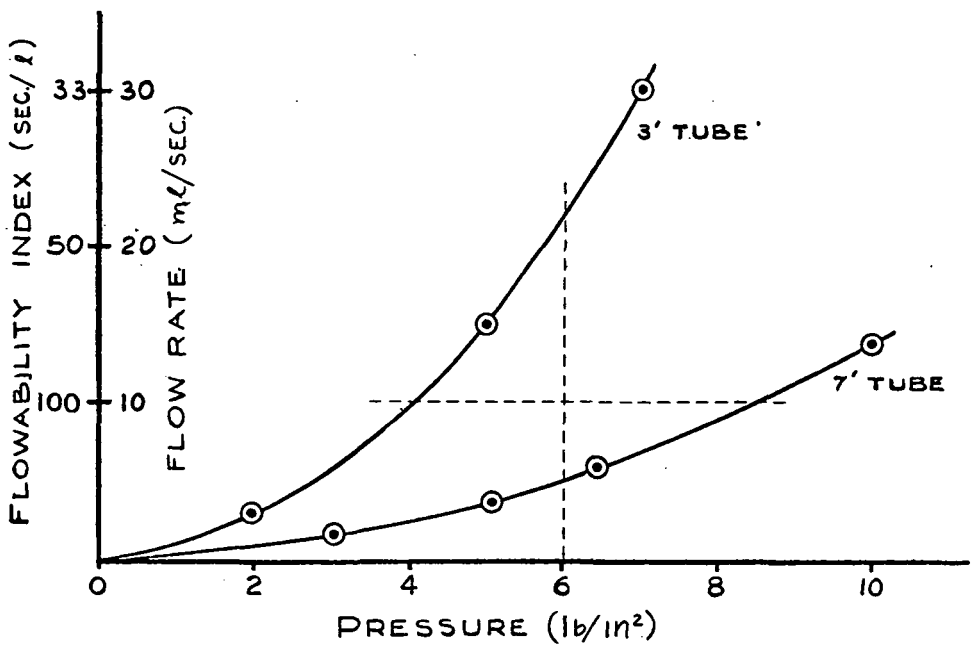


ABSORPTION TEST

FLOW OF GELGARD® POLYMER IN 3/8" I.D. TUBING

POLYMER 2.5% IN 5% SODIUM CHLORIDE

2.



attached delivered at 50 psi, 3000 ml/sec. of a gel which in the gel tester gave a flow 100 ml/sec. at 10 psi. Using Poiselle's Law for a Newtonian fluid, the rate of flow in the larger pipe should be 200 times larger than in the small pipe. In fact it is only 30 times larger in this example due to the non-Newtonian character of the fluid. In another study where the pressure in the flowability tester was reduced to 5 psi, the flow rate in the hose was found to be 240 times greater than in the tester, a much closer agreement. The flowability tester as presently developed will not permit direct correction for tube diameter. The correlation must be established empirically. The tester may be used to compare the flowability of various gels.

2. Absorption

Static absorptions were conducted with the apparatus shown in Figure 1. The nitrogen tetroxide or Aerozine 50 was injected by hypodermic syringe under the gel containing various reagents. The absorption was followed by disappearance of the nitrogen tetroxide color or by appearance of the characteristic purple of crystal violet when the aqueous gel contacted the Aerozine-50 containing the dye.

The amount of N_2O_4 absorbed was determined by titration of gel-nitrogen tetroxide mixtures with 1 M sodium hydroxide to a pH of 9. This procedure was applied to unbuffered gels and to gels containing sodium acetate plus acetic acid, or disodium citrate. The procedure did not work with disodium citrate because the nitrogen tetroxide appeared to oxidize as well as protonate one or more of the citrate moieties. The result for this system was finally obtained by collecting the gas evolved through the gel. A 4" conical funnel was inverted over the test dish and connected to a 1" diameter bubbler packed with 1/4" glass beads to a height of 10". The bubbler contained 50 ml. of 0.5 M sodium hydroxide. Air was drawn through the system at a rate of $\sim$2 l/min. The contents of the bubbler were back titrated with 0.5 M hydrochloric acid.

No quantitative measurements were made on the efficiency of Aerozine-50 absorption. Qualitatively it was observed that Aerozine-50 penetrated the 3.5% gel containing acetic acid-acetate buffer by diffusion. This mixing is very slow. The Aerozine-50 reacted readily with the gel-buffer system when the mixture was stirred.

b. RESULTS

The Planning Report (loc. cit.) called for the screening of the hydroxides of magnesium, lithium, sodium, and calcium. Due to difficulties experienced in the nitrogen tetroxide absorption test, the list of scavengers was extended to much weaker bases. The results of these tests are shown in Table 2. The concentration of the base or buffer system is shown in the second column, the concentration of GELGARD® polymer in the third column, and the pH of the resulting mixture in the fourth column.

TABLE 2

EVALUATION OF VARIOUS BASES AND BUFFER SYSTEMS

Base or Buffer				Slump (in./in.)[a]				Flowability		N_2O_4
				No Acetone		With 10% Acetone		Sec./Liter @ 10 psi		Absorb.
Kind	Conc'n. (M)	GELGARD® Polymer (%)	pH	1 Min.	5 Min.	1 Min.	5 Min.	25°C	50°C	23°C
$Mg(OH)_2$	3.24[b]	3	9.4	0.2	0.2	0.2	0.2	30	—	Blow Through
	0.81[c]	2.5	9.3	0.4	0.4	—	—	—	—	—
LiOH	3.24	3	12.4	0.2	0.13	0.09	0.06	43	25	Blow Through
NaOH	3.24	3	13.5	0.2	0.13	0.13	0.08	135	87	Blow Through
$Ca(OH)_2$	3.24[d]	4.5	8.5	—	Collapsed Gel - Weeps					
Na_2SiO_3	3.24	3.5	11.2	0.3	0.22	0.3	0.22	68	(e)	Solidified
$NaCO_2(CH_2)_2CO_2H$	3.24	2	4.8	—	Crystallizing Out at 23° & 0°					Solidified
$NaCO_2CH_3$+HCO_2CH_3	3.24 Each	3.5	5.0	0.15	0.15	0.15	0.15	54	—	Some Fume
Na_2 Citrate	3.24	3.5	4.7	0.15	0.15	0.15	0.15	55	—	Slight Fume

[a] Slump values are the ratio of the height to radius of spread of 1 liter of gel.

[b] Contained 3% $MgCl_2$ to prevent liquifaction of gel upon addition of acid.

[c] Contained 1% $MgCl_2$ to prevent liquifaction of gel upon addition of acid.

[d] Contained 5% $CaCl_2$ to prevent liquifaction of gel upon addition of acid.

[e] Thickened when warmed.

Systems containing the slightly soluble hydroxides of calcium and magnesium also contained the respective chlorides. These additions are necessary to supply enough soluble salts in the system to suppress the swell volume of the gel to approximately that which will exist when most of the base has been neutralized by nitrogen tetroxide. The other bases and salts are sufficiently soluble that this precaution is unnecessary. Slump values are shown in the next 4 columns. Slump values were measured after the gels reached equilibrium swell volume (approximately 2 hrs. at 23°C). Slump values of 0.1 to 0.2 were considered to be optimum. Adjustments in gel content were made by intervals of 0.5%. The experiments with acetone were run to simulate the effect of an organic additive. The flowability index was measured once the desired slump was obtained. Low values of this index are preferred. The absorption of N_2O_4 injected under a layer of gel was examined qualitatively on all systems of interest. These results are shown in the last column of Table 2.

Table 3 shows the results of more extensive studies of the absorption of nitrogen tetroxide in various systems and includes details of the effect of the temperature of the absorption system. The composition of the system is described in the first three columns of Table 3. The approximate pH is given in the fourth column. The quantities of absorbent mixture and of nitrogen tetroxide injected under the absorbent mixture are given in the fifth and sixth columns. The temperature of the absorption system is shown in the seventh column. The percentage of nitrogen tetroxide absorbed as determined by the titration procedure except for the citrate system is shown in the last column.

c. DISCUSSION

The proposal to use strong bases to scavenge nitrogen tetroxide is not new (2). However, the combination of a base and a gelling agent and the role of the base strength in suppressing the evolution of gaseous oxides of nitrogen have not been examined previously. The presence of a base to neutralize nitric and nitrous acids is essential to prevent the decomposition of the latter to nitric oxide which is insoluble in water and evolves from the system. Additionally, the gel must be protected against persistent high acidity which will cause it to collapse. The critical lower pH is 4.1 in an acetic acid-acetate buffer initially 1M in each component.

Sodium hydroxide, lithium hydroxide, magnesium hydroxide, and calcium hydroxide were screened first (Table 2). The calcium hydroxide gel containing 5% added calcium chloride completely dehydrated and collapsed due to the formation of the insoluble calcium salt of the polymer gel. Of the three remaining candidates the magnesium hydroxide containing gel, which was only partially hydrated, gave by far the best flowability for a given slump, showed no tendency for the slump to continue after one minute, and showed no sensitivity to addition of acetone. However,

the gel failed to absorb nitrogen tetroxide which boils at 21°C. At the contact between the gel containing magnesium hydroxide and the nitrogen tetroxide the latter boiled violently like a drop of water on a hot stove. Similarly, the fully hydrated gels containing lithium or sodium hydroxides exhibited interfacial boiling when contacted with nitrogen tetroxide. The heat was presumed to come from the reaction of liquid nitrogen tetroxide with hydroxyl ion.

	N_2O_4	+ $2OH^-$	→ NO_2^-	+ NO_3^-	+ H_2O	(1)
$\Delta H°$(kcal/g mole)	-4.7(l)	-55.0(aq)	-25.4(aq)	-49.4(aq)	-68.3(l)	
(3,4)	-4.7(l)	-110.0(aq)	-25.4(aq)	-49.4(aq)	-68.3(l)	

Net $\Delta H° = -28.4$ kcal/g mole N_2O_4

A crude experiment was run to check this result. Ten ml. of nitrogen tetroxide was injected slowly into 500 ml. of 1M sodium hydroxide cooled to 10°C in a 1 pint Dewar flask. The total temperature rise was 9° corresponding to a ΔH of -32 kcal/g mole for reaction (1).

To reduce the heat of reaction weaker bases were tested against nitrogen tetroxide. The bases had to be strong enough to neutralize nitrous acid. The surfaces of gels containing sodium silicate or the monosodium salt of succinic acid solidified when the corresponding insoluble acids precipitated in contact with nitrogen tetroxide. This prevented any further contact of the still active portion of the gel with the spill and also prevented the healing of blow holes in the gel. Sodium acetate, the conjugate base of acetic acid, combined with acetic acid to trap the fuel components, gave a gel with excellent physical properties which would absorb the nitrogen tetroxide without violent boiling. High acidity actually collapsed the gel at the interface, rapidly freeing additional acetate ion, which reduced the acidity and permitted gel to reswell. The reaction of acetate ion with nitrogen tetroxide is assumed to be

	N_2O_4	+ $2CH_3COO^-$	+ H_2O	→ NO_2^-	+ NO_3^-	+ $2CH_3COOH$	(2)
$\Delta H°$(kcal/g mole)	-4.67(l)	-116.84(aq)	-68.32(l)	-25.4(aq)	-49.37(aq)	-116.74(aq)	
(3,4)	-4.67(l)	-233.68(aq)	-68.32(l)	-25.4(aq)	-49.37(aq)	-233.48(aq)	

Net $\Delta H° = -1.6$ kcal/g mole N_2O_4

An experiment with 1M sodium acetate and 1M acetic acid in place of 1M sodium hydroxide was run. The net temperature change was 1.2°C corresponding to an enthalpy change of -4 kcal. The fact that both predictions are low by ~3 kcal suggests that one or more of the enthalpy values for the nitrogen oxide system is in slight error. The free energy change for the nitrogen tetroxide-sodium acetate reaction was calculated to be -4.25 kcal/g mole N_2O_4 which is sufficient to drive the reaction to essential completion as written. Experimentally, the pH of a 1M solution of sodium acetate reacted with 65% of the theoretical amount of nitrogen tetroxide gave a measured pH of 4.6 (calculated pH 4.5) with no corrections for the activities of the various species. The pH would have been much lower if the reaction had been incomplete. These results demonstrate that the acetate ion will react with nitrogen tetroxide without the release of a large amount of heat at the interface and, as a consequence, interfacial boiling is suppressed. Disodium citrate was entered into the screening program at the request of the monitor. The acid form of this salt is non-volatile. No thermochemical data are available, but this compound did give gels which would trap nitrogen tetroxide. These gels were much more sticky than those made with the acetate system due to the stickiness of disodium citrate solution.

Sodium carbonate was not screened as a scavenger for nitrogen tetroxide in spite of the fact that the calculated enthalpy for the reaction of 1 mole of nitrogen tetroxide and 1 mole of sodium carbonate is only -2.5 kcal. This reagent causes the evolution of carbon dioxide which will disrupt the gel layer. In addition, vaporization of the nitrogen tetroxide is promoted by the sweeping effect of carbon dioxide as it is evolved. Henderson (5) reported a negative result in large scale tests with sodium carbonate dissolved in water.

A search of the unclassified files at Ames Laboratory, NASA, failed to disclose any prior studies of interfacial boiling when nitrogen tetroxide was contacted with water. It has been noted that the occurrence of explosions when hydrazine and nitrogen tetroxide were forcefully mixed were not particularly dependent upon the temperature of the system (6). However, the authors did emphasize that the mixing produced immediate and violent boiling of liquid nitrogen tetroxide and that the reaction could be completely stopped by the evolving gas ejecting the hydrazine from the reaction zone.

The recognition of interfacial boiling as a critical factor made the proposed absorption experiments at 50° meaningless. Instead, a series of quantitative absorption experiments was run at room temperature (23°C) and at 0°C. The results of these experiments are shown in Table 3. Water alone at 23°C was only 30% efficient but cracked ice and water absorbed the nitrogen tetroxide quantitatively. Unfortunately there is no convenient method of putting ice cubes on a hypergolic fire. Predictably the sodium hydroxide failed completely at 0°C. The 3.24 M acetate system without gel was 100% efficient at 0°C even when challenged

TABLE 3

QUANTITATIVE STUDIES OF N_2O_4 ABSORBTION

Base or Buffer							
Kind	Conc'n. (M)	GELGARD® Polymer (%)	pH	Amount of Gel (ml.)	N_2O_4 (ml.)	Temp. °C	N_2O_4 Absorbed (%)
None		None	~7	100	10	23	30
		None	~7	100	10	0 (Ice)	100
NaOH	3.24	None	~13	100	10	0	Blow Through
NaO_2CCH_3+ HCO_2CH_3	3.24 Each	None	~5	100	10	23	30
		None		100	10	0	100
		3		100	2	0	100
		3		100	10	0	90
	0.81	3		100	10	0	79
Na_2 Citrate	3.24	3	~5	100	2	0	No Fume[a]
		3		100	4	0	" "
		3		100	7	0	" "
		3		100	5	0	85

[a] Titration procedure inaccurate.

with an equimolar quantity of nitrogen tetroxide but showed low efficiency at 23°C. With gel present at 3% the efficiency dropped to 90%. A cold, 0.81 M acetate system was challenged with four times the stoichiometric amount of nitrogen tetroxide and was able to retain 79% of the material. This is an extremely severe test which caused the gel to liquify. The experiments with disodium citrate failed to give quantitative answers using the direct titration procedure. However, one experiment with half the stoichiometric amount of nitrogen tetroxide using the adsorption procedure showed 85% absorption, somewhat inferior to the acetate system but certainly acceptable.

On the basis of these results the recommendation was made to test a 3% polymer gel containing 0.5 to 3.24 M sodium acetate and a similar amount of acetic acid. Subsequent field experience has shown that 3.5% polymer is better.

Part C: SCAVENGING AGENTS FOR HYDRAZINE AND UDMH

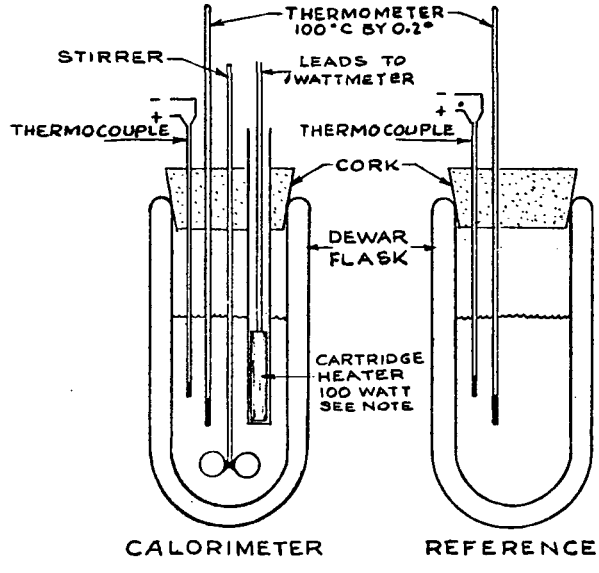
a. EXPERIMENTAL

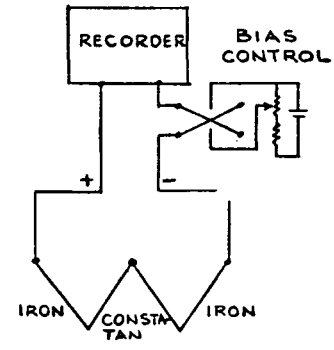
A calorimeter was built from two Dewar flasks as shown in Figure 3. The recorder for the screening studies was an L&N Model H equipped with a 1 mv. card and having a 3 second response time. For the kinetic studies this instrument was replaced by a Honeywell Electronik 19 multirange recorder which was operated at appropriate sensitivity as high as 0.2 mv. full scale. The response time of this recorder was 1/8 sec. To minimize thermocouple lag, 1/16" diameter stainless steel units having an i.c. junction in the tip (Model TT-3Y, Harco Labs Inc., Branford, Conn.) were used. A cartridge heater for calibration purposes was incorporated in the original design. A wattmeter of sufficient precision was not available so the calorimetric constant of the unit was finally determined by neutralizing 250 ml. of sodium hydroxide (0.5M) with 250 ml. of hydrochloric acid (0.5M). The measured constant was 0.877 deg/cal/ml. This value only applied when the volume of solution in the flask was 500 ml. The reference junction was normally maintained at the starting temperature for the experiment. Bias control was obtained with a potentiometer made from a 100 ohm Helipot in series with a 33K ohm resistor and a mercury battery.

b. RESULTS

The study breaks down into 3 parts -- screening of potential reagents, detailed kinetic studies and compatibility of the gel with additives with the fuel components.

CALORIMETER





THERMOCOUPLE CIRCUIT

NOTE CARTRIDGE HEATER AND GLASS ENVELOPE ARE REMOVED TO PERMIT ADDITION OF REAGENTS

The screening was done using the calorimeter. Reactions which have significant negative enthalpies (nominally $\geq$-3.6 kcal/g mole) and which were essentially complete in 15 minutes or less with 1 molar concentration of reactants were sought. The list of reagents to be screened based upon a review of the open literature was given in the Planning Report (1). All screening was done in acetic acid-sodium acetate buffer as a consequence of the findings in Part B. The buffer used in the hydrazine experiments was 1.76M in acetic acid and 1.88M in sodium acetate. The hydrazine was 1.54M. The buffer used for the UDMH screening was 1.23M in acetic acid and 1.31M in sodium acetate. The UDMH was 1M. Scavenging agents were 1M in both series of experiments.

In all cases the hydrazine component was mixed with 300 ml. of buffer and the scavenger with 200 ml. of buffer. Stock solutions of 5M UDMH in buffer could not be prepared as was done with hydrazine because the UDMH-acetate salt crystallized out. Solutions of 2.5M UDMH did not crystallize. The stock solutions of hydrazine and UDMH contained insufficient acid to completely neutralize the fuel component. The exotherm on mixing the hydrazine buffer combination with the rest of the buffer was 3.4°C and for UDMH 2.8°C. These exotherms were discounted in determining if a significant heat of reaction existed between the fuel component and the scavenger.

The results of the screening experiments are summarized in Table 4. The reagent is shown in column 1. Pseudo second order rate constants for the hydrazine and UDMH systems are shown in the second and third columns. These constants are based on the half time of reaction and assume the reaction is second order and the stoichiometry is 1:1 mole basis. The pseudo second order constant for the hydrazine case was obtained by solving the equation $kt = \frac{2.303}{(a-b)} \log \frac{b}{a} \frac{(a-x)}{(b-x)}$ for k using for a, the initial amount of scavenger, 1.00; for b, the initial amount of hydrazine, 1.54; and for x, the molar concentration of product formed, 0.5. For the UDMH system the equation $kt = \frac{1}{a} \frac{x}{(a-x)}$ was solved for k using a = 1.0 and x = 0.5. The adiabatic molar enthalpies of reaction are shown for hydrazine and UDMH in the fourth and fifth columns. The values were obtained by dividing the net temperature rise, after correction for any heat of neutralization, by the calorimetric constant and multiplying the result by the ratio of the volume of the system to the moles of reagent present in least amount, i.e., adiabatic enthalpy = $\frac{(\text{net}\Delta T) \times 500}{0.87_7 \times 0.5}$. The molar enthalpies are based upon the assumption of 1:1 stoichiometry. The enthalpies for 2,4-pentanedione, 1,3-cyclohexanedione, and divinylsulfone are shown as divided by two since these compounds are difunctional in all probability. The "notes" generally include the principal reason for rejecting a compound. Some toxicity data are given in the last column. The heats of neutralization of the fuel components were measured by adding 0.4 mole of fuel component in 100 ml. water to 400 ml. of 1.25M

TABLE 4

PRELIMINARY SCREENING OF SCAVENGERS FOR HYDRAZINE AND UDMH[a]

Scavenger	Pseudo Second Order Rate Constant ($M^{-1}min.^{-1}$) N_2H_4	UDMH	Adiabatic $-\Delta H$ (kcal/g mole) N_2H_4	UDMH	Notes	Toxicity[b]
Formaldehyde	4	0.2	13	14	N_2H_4 adduct smelled like ether.	Rat, LD_{50} 0.8g/kg.o.
Acetaldehyde	>9	<0.2	10	3	Adduct smelled like ether.	Rat, LD_{50} 1.9g/kg.o.
Salicylaldehyde	0.2	--	14	<3	Reagent not soluble.	Rat MLD 1.09g/kg.
Cyclohexanone	>9	--	7	<3	Reagent not soluble.	Rat LD_{50} 1-10g/kg.o.[c]
Butanone-3-al	(See corresponding acetal, next line.)					
4,4-Dimethoxy-2-butanone	5	--	8	<3	Products smell. No Rx UDMH.	--
2,4-Pentanedione	>9	2	38/2	15/2	UDMH product smells.	Rat LD_{50} 0.1-1g/kg.o.[c]
1,3-Cyclohexanedione	3	--	13/2	<3	N_2H_4 product colored. No Rx UDMH.	--
1,4-Cyclohexanedione	--	--	--	--	Too expensive ($10.75/10g).	--
Methyl Formate	5	--	3	<3	No Rx.	Rat LD_{50} 0.1-1g/kg.o.
Acetyl salicylate	--	--	<3	--	Reagent not soluble.	--
Methyl pyruvate	1	--	7	--	Too expensive ($33.60/100g).	--
Methyl acetoacetate	4	--	21	--	High equivalent weight.	Rat LD_{50} 3g/kg(o.?)
Propiolactone	2	0.6	22	19	Toxicity.	Labeled carcinogenic.
γ-Butyrolactone	>9	--	3	<3	No Rx with UDMH.	--
γ-Thiovalerolactone					Not available.	--

TABLE 4 (cont.)

Scavenger	Pseudo Second Order Rate Constant ($M^{-1}min.^{-1}$) N_2H_4	UDMH	Adiabatic $-\Delta H$ (kcal/g mole) N_2H_4	UDMH	Notes	Toxicity[b]
Acrolein	--	--	--	--	Toxicity.	Rat, LD_{50} 0.03g/kg s.c.
Succinonitrile	>9	--	5	<3	No Rx with UDMH.	Rat, LD_{50} 450g/kg.o.
Methylvinylketone	>9	>9	25	16	Toxicity.	Very lachrymatory.
Divinylsulfone	0.5	>9	38/2	15/2	Toxicity.	--
N-vinylpyridinium-fluorborate	--	--	--	--	Not available.	--
Trimethylvinylammonium salt	--	--	--	--	Too expensive ($18.00/10g).	--
Trimethylvinylphosphonium salt	--	--	--	--	Not available.	--
β-Chloroacrylonitrile	--	--	--	--	Not available.	--
1,2:3,4 Butadienedioxide	>9	--	5	--	Post-reacted (polymerized?)	LD_{50} 0.088g/kg(o.?)[e]
Succinic anhydride	>9	--	5	<3	No Rx with UDMH.	Moderate[d]

Notes:

(a) All results are from single experiments and are not corrected for non-aqueous diluents or temperature effect.

(b) P.G. Stecher, Ed., The Merck Index, 8th Edn., Merck & Co. Inc., 1968. Except

(c) N.V. Steere, Ed., Handbook of Laboratory Safety, 2nd Edn., The Chemical Rubber Co., Cleveland, 1970.

(d) N.I. Sax, Dangerous Properties of Industrial Materials, 3rd Edn., Van Nostrand Reinhold New York, 1968.

(e) H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw Hill, New York, 1967.

buffer. Heats of solution were taken from literature where available. The temperature rises to be expected from mixing Aerozine-50 with the scavenging mixtures in various ratios are shown in Table 5. The heat capacity of the extinguishant system was assumed to be identical with an equivalent volume of water. The first two columns give the grams of extinguishant and volumetric ratio of extinguishant to 1 mole of Aerozine-50. One mole of Aerozine-50 weighs 39 grams. The heats of solution in column 3 were based on the published data for hydrazine. The heat of neutralization in column 4 was measured. The identity and concentration of scavenger appear in columns 5 and 6. The heats of reaction in column 7 were obtained from the data of Tables 6-9 rather than from Table 4. The calculated temperature rises of each fuel extinguishant system are shown in the last 4 columns.

The kinetic studies were conducted in the same calorimetric setup as the screening experiments. According to plan, two reagents were selected for evaluation. The 2,4-pentanedione was the reagent of choice based on the vigorous reaction found during screening. Formaldehyde was the second choice. Four experiments were planned for each combination of scavenger and fuel component. Additional experiments were performed where the original four experiments failed to give a clear kinetic picture. The entire sequences of experiments for hydrazine were repeated at lower concentrations than were originally planned because the reactions were too fast. The data for the original sets using 0.8M reagents are not shown since they have no significance. In all cases, the hydrazine or UDMH was mixed with 300 ml. of the 1M buffer and the scavenger with the remaining 200 ml. In those experiments with 0.8M UDMH, a small temperature rise of 2.0 to 2.2°C was observed upon mixing the scavenger solution. This heat was due to incomplete neutralization of the 0.8M UDMH in the 300 ml. of 1M buffer.

Rate constants from these studies were derived by reading time vs. temperature from the recorder plotted data. Conversions were obtained by assuming conversion was proportional to the fraction of the total observed temperature rise. The activation energy (the E of the Arrhenius Equation) was calculated by plotting time vs. conversion curves for the equimolar reactions started at nominal temperatures of 15°C and 25°C. Relative times were compared at 50% and 75% conversion. This procedure is valid because kt, the product of the rate constant and the time required to reach a given conversion is a constant for two reactions equivalent in all respects except starting temperature. The calculations are detailed in Appendix A, Kinetic Data 1. The values obtained at 50% and 75% conversion were averaged. The values so obtained also appear in column 3 of Tables 6-9. Also shown in Tables 6-9 are the results of the rate constant calculations taken from Appendix A, Kinetic Data and the associated rate plots. The references in Tables 6-9 refer to the Tables of Kinetic Data which in turn are referenced to the associated rate plot.

TABLE 5

ESTIMATED TEMPERATURE RISE UPON REACTION OF 1 MOLE OF AEROZINE-50 WITH EXTINGUISHANT SYSTEMS

Extinguishant System: Water Containing 1 Mole Each of Acetic Acid and Sodium Acetate Plus a Scavenger

Extinguishant Weight g	Extinguishant Ratio to Fuel	Heat of Solution (kcal/g mole)	Heat of Neutralization (kcal/g mole)	Scavenger Identity	Scavenger Conc'n. (M)	Heat of Reaction[a] with Scavenger (kcal/g mole)	ΔT(°C) Solution	ΔT(°C) Neutralization	ΔT(°C) Scavenger	ΔT(°C) Total
18	0.46:1	-1.8	-10	2,4-PD	1	-25.7	43	4	11	58
				HCHO	2	-15.7	43	4	13	60
390	10:1	-3.9	-10	2,4-PD	1	-25.7	9	9	24	42
				HCHO	2	-15.1	9	9	28	46
1570	40:1	-3.9	-10	2,4-PD	1	-25.7	2	6	16	24
				HCHO	2	-24.62	2	6	31	39

NOTE: [a] Weighted averages based on data from Tables 6-9.

TABLE 6

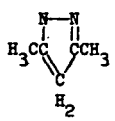
HYDRAZINE AND 2,4-PENTANEDIONE

Rate Law:

$$kt = \frac{1}{a}\frac{x}{(a-x)} = \frac{2.303}{a-b}\log\frac{b}{a}\frac{(a-x)}{(b-x)}$$

Verified Path:

$$H_2NNH_2 + CH_3COCH_2COCH_3 \xrightarrow{k}$$



$+2H_2O$

Rate Constants:

Conc'n. of Reactants(M) H_4N_2	Conc'n. of Reactants(M) 2,4-PD	Activation Energy (kcal/g mole)	Rate Constants M^{-1} $min.^{-1}$ Uncorr.	Rate Constants M^{-1} $min.^{-1}$ pH corr.	ΔT °C	Ref. Table
0.2	0.1		79	79	2.7	A5
0.1	0.2		63	74	2.5	A4
0.2	0.2	8.8	93	93	5.3	A2
0.2	0.2		97	97	5.4	A3
0.2	0.2 (3.5% gel)		116	95	6.2	A6
				Avg. 88		

ΔH_{av} = -31 kcal/g mole

TABLE 7

UDMH AND 2,4-PENTANEDIONE

Rate Law:

$$kt = \frac{1}{a}\frac{x}{(a-x)} = \frac{2.303}{a-b}\log\frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{(a-0.5b)}\log\frac{b}{a}\frac{(a-0.5x)}{(b-x)}$$

Verified Path:

$$Me_2NNH_2 + CH_3COCH_2COCH_3 \underset{?}{\rightleftharpoons} Me_2NN{=}C(CH_3)CH_2COCH_3 + H_2O$$

$$Me_2NNH_2 + Me_2NN{=}C(CH_3)CH_2COCH_3 \underset{?}{\rightleftharpoons} Me_2NN{=}C(CH_3)CH_2C(CH_3){=}NNMe_2 + H_2O$$

Rate Constants:

Conc'n. of Reactants (M)		Activation Energy	Rate Constants ($M^{-1}min.^{-1}$)				ΔT	Ref.
			1:1 Stoich.		2:1 Stoich.			
Me_2NNH_2	2,4-PD	(kcal/g mole)	Uncorr.	pH Corr.	Uncorr.	pH Corr.	°C	Table
0.8	0.4		0.57	0.57	Curved		4.6	A9
			0.42	0.55	0.39	0.51	3.9?	A10
0.4	0.8		Curved				4.5	A11
			0.28	0.37	0.25	0.33	4.6	A12
0.8	0.8	6.2	0.76	0.76	0.55	0.55	10.0	A7
0.8	0.8		0.88	0.88	0.55	0.55	10.0	A8
0.4	0.4		0.37	0.49	0.23	0.30	4.1	A13
			Avg.	0.60				

ΔH_{av} = -13 kcal/g mole

TABLE 8

HYDRAZINE AND FORMALDEHYDE

Rate Law:

$$kt = 2.303 \log \frac{a}{a-x}$$

Suggested Path:

$$H_2NNH_2 + HCHO \rightleftharpoons H_2NNHCH_2OH$$

$$H_2NNHCH_2OH \xrightarrow{k_1} H_2NN{=}CH_2^* + H_2O$$

$$H_2NN{=}CH_2 + HCHO \rightleftharpoons HOCH_2NHN{=}CH_2$$

$$HOCH_2NHN{=}CH_2 \xrightarrow{k_2} CH_2{=}NN{=}CH_2 + H_2O$$

Note* This species may be an alternating polymer.

Rate Constants:

Conc'n. of Reactants (M)		Activation Energy	Rate Constant M^{-1} $min.^{-1}$		ΔT	Ref.
H_4N_2	HCHO	(kcal/g mole)	Uncorr.	pH Corr.	°C	Table
0.4	0.2		2.7	3.2	1.64	A16
0.2	0.4		2.5	2.5	3.43	A17
			1.3(second step)			
0.2	0.2	16.5	2.8	2.8	1.60	A14
0.2	0.2		3.0	3.0	2.00	A15
				Avg. 2.9		

$$\Delta H_{av} = -9.8 \text{ kcal/g mole}$$

TABLE 9

UDMH AND FORMALDEHYDE

Rate Law:

$$kt = \frac{1}{a}\frac{x}{a-x} = \frac{2.303}{a-b}\log\frac{b}{a}\frac{(a-x)}{(b-x)} \text{ (Approximately)}$$

Suggested Path:

$$Me_2NNH_2 + HCHO \longrightarrow Me_2NNHCH_2OH \xrightarrow{k} Me_2NN{=}CH_2 + H_2O$$

Excess HCHO (?)

$$Me_2NNH_2 + xHCHO \longrightarrow\longrightarrow (Me_2NN\cdot xHCHO)_y \text{ polymer}$$

Rate Constants:

Conc'n. of Reactants (M)		Activation Energy	Rate Constants M^{-1} min.$^{-1}$		ΔT	Ref.
UDMH	HCHO	(kcal/g mole)	Uncorr.	pH Corr.	°C	Table
.4	.8		0.16	0.21	12.5, 11.9	A22
.8	.4		0.037	0.037	8.4	A20
.8	.8	19.2	0.19	0.19	15.1	A18
.8	.8		0.20	0.20	15.1	A19
.8	1.6		0.067	0.067	24.0	A21
.4	1.6		0.047	0.062	17.3	A23

Representative Rate Constant=0.06M^{-1}min.$^{-1}$

Maximum ΔH $\geq$ -24 kcal/g mole UDMH

Minimum ΔH = -24 kcal/g mole UDMH

The raw data for the Kinetic Data Tables were obtained by reading temperatures off the recorder curves at selected times. The temperatures were converted to molar conversion with respect to the minor component by taking the ratio of the temperature rise at a given time to that at infinite time and multiplying by the initial concentration of the minor component. The amount of each component remaining was calculated by subtracting the amount converted from the initial amount with appropriate corrections for stoichiometry. The appropriate variable term for the rate law being tested was calculated and is shown in the last column(s).

Temperature corrections were made by expanding the time scale by a factor expKx where K is calculated from activation energy data given in Kinetic Data Table 1 and x is the molar conversion. If the temperature range of the experiment exceeded 8°C the values of the corrected time exceed an error of 2% and K was recalculated for each time interval. Data were plotted on appropriate scales to obtain the rate plots included in Appendix A. The rate constants derived from these plots are shown at the foot of each table along with a reference to the figure. All constants were corrected to 25°C using the Arrhenius Equation.

The pH correction was required for some systems due to a change in buffer pH with fuel component concentration. The correction is derived as follows:

Let Hyd be the molar concentration of the unprotonated fuel component.

H^+Hyd be the molar concentration of the protonated fuel component.

c be the stoichiometric concentration of the fuel component in all forms.

d be the initial molar concentration of acetic acid (HOAc).

e be the initial molar concentration of the sodium acetate (OAc^-).

Then for a mixture of a fuel component with excess buffer

$$[Hyd] = c-[H^+Hyd]$$

$$[H^+Hyd] = c-[Hyd]$$

$$[HOAc] = d-c+[Hyd]$$

$$[OAc^-] = e+c-[Hyd]$$

$$\frac{[H^+][OAc^-]}{[HOAc]} = 1.8\times10^{-5} = \frac{[H^+]([e+c-[Hyd])}{d-c+[Hyd]}$$

$$[H^+] = \frac{1.8\times10^{-5}(d-c+[Hyd])}{e+c-[Hyd]}$$

For hydrazine

$$\frac{[H^+][Hyd]}{[H^+Hyd]} = 5.75\times10^{-9} = \frac{[H^+][Hyd]}{c-[Hyd]}$$

$$[H^+] = \frac{5.75\times10^{-9}(c-[Hyd])}{[Hyd]}$$

Since $[H^+]$ must be the same for both equations

$$\frac{1.8\times10^{-5}(d-c+[Hyd])}{e+c-[Hyd]} = \frac{5.75\times10^{-9}(c-[Hyd])}{[Hyd]}$$

But $[Hyd] \ll c$ in systems of interest

$$[Hyd] = \frac{5.75\times10^{-9}c(e+c)}{1.85\times10^{-5}(d-c)}$$

For solutions involving UDMH the dissociation constant 5.75×10^{-9} is replaced by 2.75×10^{-8}. For one experiment involving the gel the effective value of c was increased by basic components in the polymer.

Identifications of products obtained in the detailed kinetic study were obtained by infrared spectrometry or nuclear magnetic resonance spectrometry (NMR). The vapor phase chromatography (VPC) was not attempted because the prognosis determined after a discussion with Varian Associates, was poor.

Absorption experiments were conducted in the previously described conical bottom dish.

c. DISCUSSION

1. Selection of Scavengers for Detailed Study

The criterion for vigorous reaction is an adiabatic enthalpy decrease in excess of -3 kcal/g mole. The minimum acceptable decrease in enthalpy was originally set at -3.6 kcal/g mole. The criterion for rapid reaction was fixed at 10^{-2} $M^{-1}sec^{-1}$ corresponding to $\sim$0.2 $M^{-1}min^{-1}$ for an assumed second order rate constant. Under these conditions a mixture of 1M scavenger with 1M fuel component will react to 90% completion in 45 min. With 2M scavenger the reaction would be 90% complete with respect to the fuel component in 8.5 min.

Examination of the data in Table 4 shows that many of the available reagents react readily with hydrazine but only five compounds show acceptable rates with UDMH. Methyl vinyl ketone and divinylsulfone are very fast but are also very toxic. Propiolactone reacts satisfactorily but is

classed as a carcinogen. This leaves only 2,4-pentanedione and formaldehyde in order of preference. Acetaldehyde may work, but it does not meet the rate criterion.

Heats of reaction for the two scavenger systems of choice were refined in the course of the detailed kinetic study (Section C3). The heats of reaction for the systems with 2,4-pentanedione were slightly lower than indicated by the screening values. The reaction of hydrazine with formaldehyde also gave a lower value but a side reaction, believed to be a polymerization reaction, caused the heat of reaction of formaldehyde and UDMH to increase with increasing excess of formaldehyde.

In addition to the heat liberated by the scavenger reaction, the heat of solution of the fuel components in water, and the heat of neutralization of the fuel components must be taken into account. The heat of solution of hydrazine to give monohydrate is -1.8 kcal/g mole and for a dilute solution -3.9 kcal/g mole (7). The heat capacity of hydrazine at 25°C is 23.6 cal/mole/deg. (8) and of water 18 cal/mole/deg. The heat of solution and heat capacity of UDMH are not known but since the molar heat capacity would be expected to increase and the heat of neutralization to decrease in comparison with hydrazine it was assumed that the molar heat capacity of hydrazine would be a fair representation of UDMH behavior. Based on these assumptions 1 mole of Aerozine-50 having 0.75 mole hydrazine and 0.25 mole of UDMH has an apparent molecular weight of 39, a molar heat capacity of 23.6 cal/mole/deg., and a heat of solution of -1.86 to -3.9 kcal/mole.

The neutralization of the fuel components by acetic acid follows the reactions

$$N_2H_4 + CH_3COOH \rightarrow N_2H_5^+ + CH_3COO^- \qquad \Delta H = -11.3 \text{ kcal/g mole}$$

$$Me_2N_2H_2 + CH_3COOH \rightarrow Me_2N_2H_3^+ + CH_3COO^- \qquad \Delta H = -6.0 \text{ kcal/g mole}$$

The heats of neutralization were obtained experimentally. They could not be calculated theoretically because heats of formation were not available for the protonated fuel components.

The total temperature rise to be expected upon mixing 1 mole of Aerozine-50 with various amounts of extinguishant were calculated for the two scavenger systems of choice. The results appear in Table 5. The total calculated temperature rise is about 40-60°C until a molar excess of scavenging agent (1000 ml. of extinguishant) is present. The temperatures then decline for both systems but the formaldehyde system liberates relatively more heat than the 2,4-pentanedione system. Since UDMH boils at 63°C (732 mm) (9), the temperature rises are sufficient to volatilize significant amounts of UDMH. Cooling the extinguishant to 0°C would obviously be an advantage.

The results also indicate that a large excess of gel should be well mixed into the fuel component to get maximum control. If the only objective were the suppression of the vapor pressure of the fuel components, a weak acid would be the reagent of choice because of the lower heat of reaction. However, the scavenging agents do form compounds of lower reactivity and hopefully lower toxicity than the fuel components.

2. Kinetic Studies of Scavengers

(i) Hydrazine and 2,4-Pentanedione

The results for the kinetic studies of hydrazine with 2,4-pentanedione are summarized in Table 6. Both first and second order rate plots were prepared. In all cases the first order plots were curved. The second order rate constants were corrected for a pH effect. The average rate constant is 88 $M^{-1}min^{-1}$. Kinetically it appears that the unprotonated hydrazine species reacts directly with 2,4-pentanedione in a rate controlling step. However the amount of free hydrazine varies slightly with hydrazine concentration because the buffer does not have infinite capacity. The results obtained using 0.1 M hydrazine contained proportionately less hydrazine than the experiments run at 0.2 M hydrazine. The gel contained anionic carboxylate ions amounting to 0.5 M which contributed alkalinity to the buffer system equivalent to having 1.5 M instead of 1M sodium acetate. After correction for this difference the rate constant for the gel containing system is in good agreement with ungelled systems. The gel does not hinder the reaction of the hydrazine and scavenger provided the components are well mixed.

The total temperature rise data (ΔT) show that the reaction is strictly following 1:1 stoichiometry regardless of which component is in excess, consistent with the literature (10). The temperature for the system containing gel is slightly higher than expected but there is no particular significance attached to this result. The average enthalpy of reaction is -31 kcal/g mole, slightly lower than determined in the one-shot screening experiments.

The product of the reaction, 3,5-dimethylpyrazole, precipitated and was readily identified by comparing an infrared spectrum to reference spectra. This precipitate later proved to be very deleterious in the field because it skinned the gel over and prevented further contact of the still active portion of the gel and the fuel components.

(ii) UDMH and 2,4-Pentanedione

Three rate plots were prepared for the UDMH-2,4-pentanedione system. The first order plots were curved. The second order plots for 1:1 and 2:1 stoichiometry were essentially straight lines up to 80% conversion

with two exceptions. The rate constants derived from these plots are summarized in Table 7. The pH correction was applied to place all rate constants on a 0.8 M UDMH basis. The stoichiometry of the reaction under the present conditions is most probably 1:1 rather than 2:1 though it is known that the 2:1 adduct can be prepared synthetically (10).

This conclusion is based on the observation that a mixture of 0.4 M UDMH and 0.8 M 2,4-pentanedione yields the same heat (same ΔT) as a mixture of 0.8 M UDMH and 0.4 M 2,4-pentanedione. If the stoichiometry was 2:1 the mixture of 0.8 M UDMH and 0.4 M 2,4-pentanedione would have liberated approximately twice the amount of heat (assuming the enthalpy changes of the two steps are similar). There is evidence for an equilibrium reaction of the type A+B→C which is displaced 76-94% toward product in that the temperature rise for the 0.4 M UDMH plus 0.4 M 2,4-pentanedione is 82% of that for a mixture 0.8 M in each reactant and 91% of that for a mixture containing 0.4 M of one reactant and 0.8 M of the other reactant. The average of the pH corrected second order rate constants for 1:1 stoichiometry is 0.60 $M^{-1}min^{-1}$. Rate plots for equilibrium reactions were not prepared primarily because of the intractability of the expressions for unequal starting concentrations.

(iii) Hydrazine and Formaldehyde

The reaction of hydrazine and formaldehyde may give a polymeric 1:1 adduct or the monomeric bismethylene azine if a large excess of formaldehyde is present. Second order rate plots were prepared for both stoichiometries. First order rate plots with respect to the minor constituent assuming 1:1 stoichiometry were also prepared. The first order results gave the best fit and the resulting rate constants are summarized in Table 8. The fit to first order kinetics implies that the rate controlling step is the decomposition of a readily formed 1:1 adduct of formaldehyde and hydrazine to yield a hydrazone and water rather than the formation of the adduct itself (11). The temperature rise data show that the second step to give the azine also occurs but the kinetic data show the rate to be about half that of the first step. The average rate constant corrected to the 0.2 M hydrazine basis is 2.9 min^{-1}. The enthalpy of reaction is -9.8 kcal/g mole. The activation energy is very large compared to the 2,4-pentanedione systems which means that the reaction rates will be slow at 0°C. The products of reaction of hydrazine and formaldehyde came out of solution as an oil. An infrared spectrum of this oil suggested the presence of both $N=CH_2$ and $N-CH_2-N$ structures.

(iv) UDMH and Formaldehyde

The data for this system are detailed in Appendix A. The system was tested for first order and second order behavior at 1:1 stoichiometry. The second order fitted the data best but as can be seen in Table 9

the agreement of the rate constants after correction for pH to a basis of 0.8 M UDMH is very poor. The reason for this discrepancy can be seen by comparing the temperature rises for various systems. First, the 0.8 M UDMH plus 1.6 M formaldehyde system gives almost exactly twice the temperature rise as was found for 0.4 M UDMH plus 0.8 M formaldehyde. This would not occur if there was an equilibrium substantially displaced from completion. Second, the heat liberated from the reaction increases regularly with increasing formaldehyde concentration and with increasing ratio of formaldehyde to UDMH for a given UDMH concentration. This effect can only be produced by variable stoichiometry since an equilibrium reaction is ruled out by the first condition. The only logical process for the secondary reaction is some sort of polymerization of the formaldehyde which is wasteful of the scavenger. The selection of a rate constant to represent the system becomes a matter of selecting the ratio of reactants. Allowing that excess formaldehyde will ultimately be present, a value of 0.06 $M^{-1}min^{-1}$ is a conservative value. This value is lower than the 0.2 $M^{-1}min^{-1}$ originally desired.

Likewise the enthalpy of reaction cannot be stated as a single value. Using the second experiment of Table 9, which is run with the highest ratio of UDMH to formaldehyde hence will show a minimum of polymerization, the enthalpy calculates to be -12 kcal/g mole based on formaldehyde. The largest enthalpy observed in these experiments was -24 kcal/g mole for the experiment with 0.4 M UDMH and 1.6 M formaldehyde. Larger values may be observed with still larger excesses of formaldehyde.

3. Absorption of Fuel Components

The adsorption of Aerozine-50 into gel systems was examined qualitatively using a dyestuff in the Aerozine-50. Crystal violet is slightly soluble in and gives a colorless solution with the Aerozine-50, but at the contact with a buffered gel the characteristic purple color develops as the dye is protonated. Using a 3.5% buffered gel with no scavengers, it was found that the Aerozine-50 penetrated about 0.1 cm. into the gel in 20 minutes. This is essentially the rate to be expected from diffusional mixing. If the system was agitated mechanically, the mixing was much more rapid. Aerozine-50 does not actively attack the gel as does nitrogen tetroxide.

The scavenging agents for fuel components were tested for the formation of undesirable products with nitrogen tetroxide using DTA (differential thermal analysis). The acetate buffered gel containing 2,4-pentanedione after contact with a stoichiometric amount of nitrogen tetroxide showed no undesirable reactions upon heating to 360°C (Figure 4). The citrate buffered gel could not be tested because it foamed out of the cup in the apparatus, but citrate buffer less gel after contact with nitrogen tetroxide did not give any large exotherms (Figure 5).

FIGURE 4

DTA Study of Water, GELGARD® M Polymer, Acetate Buffer, 2,4-Pentanedione and Nitrogen Tetroxide System

SIZE _____
REF. _____
PROGRAM MODE _____
RATE 20 °/min, START ____ °C

ATM. air

	T	ΔT
SCALE SETTING	50 °/in	2 °/in

RUN NO. _____
DATE 9/20/71
OPERATOR Ecp

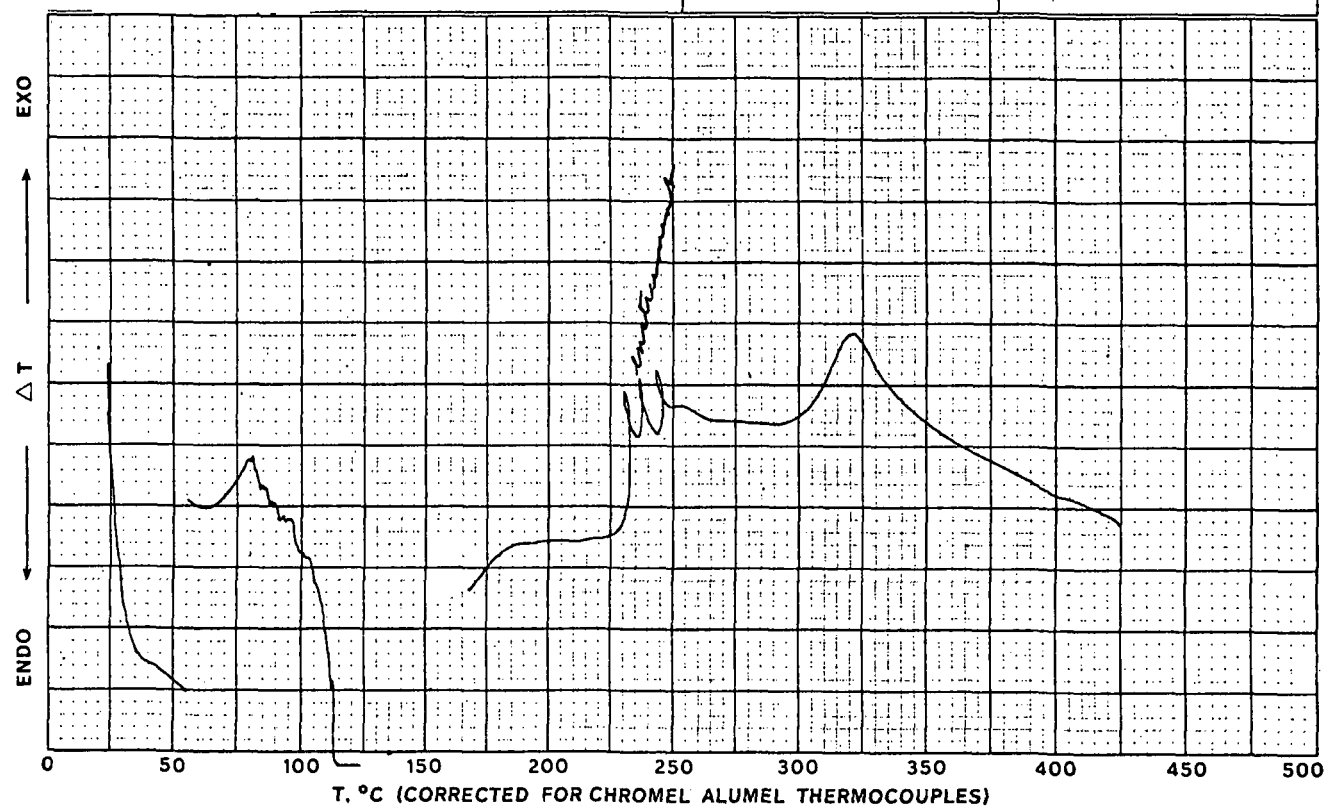


FIGURE 5

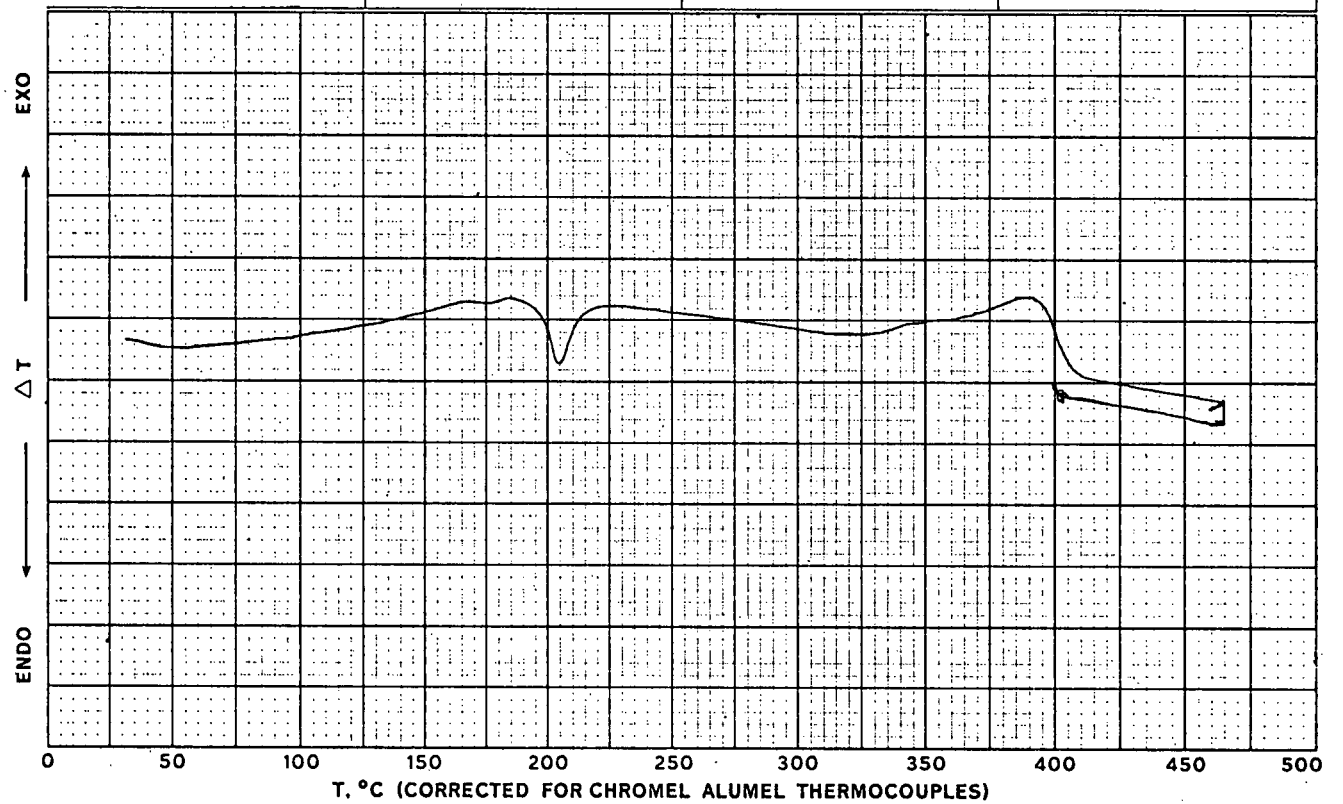
DTA Study of Water, Citrate Buffer and Nitrogen Tetroxide System

SIZE _____
REF. _____
PROGRAM MODE _____
RATE 20 °C/min, START 30 °C

ATM. air

	T	ΔT
SCALE SETTING	50	2

RUN NO. 1
DATE 9/29/71
OPERATOR ECP



The storage stability of a GELGARD® M polyacrylamide gel containing only acetate-acetic acid buffer is fair. The gel does tend to thicken on standing, and, though the slump appears to be little affected, the material does become more viscous. Extended storage of gel-buffer system in the presence of formaldehyde is not feasible. The system will only last about 3 days at room temperature before visible dewatering occurs. This is caused by the formaldehyde attacking and crosslinking the gel.

CONCLUSIONS

1. GELGARD® M polyacrylamide combined with a weakly acidic buffer to form a "pH Trap" can be used to prepare gelled water systems which, when cold, will efficiently deactivate nitrogen tetroxide and suppress evolution of nitrogen oxides. Strong bases are not acceptable for deactivating nitrogen tetroxide. The system must be kept cold to avoid boiloff of nitrogen tetroxide.

2. GELGARD® M polyacrylamide combined with a buffer system can be used to prepare a gelled water system which will blanket and absorb Aerozine-50 by diffusion and will neutralize the fuel components with a moderate evolution of heat.

3. GELGARD® M polyacrylamide combined with a buffer system will accept 2,4-pentanedione or formaldehyde additions for the purpose of deactivating fuel components.

4. The rate of reaction of 2,4-pentanedione is acceptable with both components of the Aerozine-50 as is the reaction of formaldehyde and hydrazine, but the formaldehyde-UDMH reaction is somewhat slower than desirable, nonstoichiometric, and very exothermic in the presence of excess formaldehyde.

5. Disodium citrate is a reasonable second choice for a buffer system based on incomplete data.

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APPENDIX A

KINETIC DATA A1

CALCULATION OF ACTIVATION ENERGIES

$$\ln \frac{k_1}{k_2} = -\frac{E}{R}\left(\frac{T_2-T_1}{T_1T_2}\right) = \left(\ln \frac{t_2}{t_1}\right)_x$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2

E is the activation energy in kcal/g mole

R is the gas constant (1.986 cal/deg/mole)

t_1 and t_2 are the times to reach a given conversion x.

System	Conversion (%)	t_1 (min)	t_2 (min)	T_1 (°K)	T_2 (°K)	E (kcal)	Σ_{av} (kcal)
N_2H_4 + 2,4-Pentanedione	50	0.093_3	0.055_0	290.9	300.9	9.39	8.8
	75	0.234	0.146_8	292.2	302.2	8.14	
UDMH + 2,4-Pentanedione	50	2.12	1.50	293.2	303.4	5.9_8	6.2
	75	4.7_3	3.30	295.2	305.2	6.3_2	
N_2H_4 + Formaldehyde	50	0.608	0.234	289.0	299.0	16.4_3	16.5
	75	1.150	0.442	289.4	299.4	16.4_7	
UDMH + Formaldehyde	50	11.7	4.0	297.7	307.7	19.5_0	19.2
	75	20.8	7.5	301.5	311.5	18.9_8	

KINETIC DATA A2

SYSTEM: HYDRAZINE + 2,4-PENTANEDIONE

Initial Conditions: N_2H_4 0.2M, 2,4-PD 0.2M, T_o 25°C, K = 1.31 ⚠

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$
0	0	0	0	0.200	0
1.0	1	0.10	0.003	0.197	0.015
2.1	2	0.94	0.036	0.164	0.216
3.1	3	1.78	0.067	0.133	0.505
4.3	4	2.81	0.106	0.094	1.130
5.5	5	3.19	0.120	0.080	1.508
6.6	6	3.43	0.129	0.071	1.831
7.8	7	3.64	0.137	0.063	2.19
9.1	8	3.82	0.144	0.056	2.58
11.5	10	4.06	0.153	0.047	3.28
13.9	12	4.25	0.160	0.040	4.05
16.4	14	4.43	0.167	0.033	5.10
18.9	16	4.55	0.172	0.028	6.10
21.4	18	4.63	0.175	0.025	6.97
23.9	20	4.70	0.177	0.023	7.78
26.5	22	4.79	0.181	0.019	9.42
∞	∞	5.30	0.200	0.000	∞

$$K = \frac{\frac{5.3}{0.2} \times \frac{8770}{1.986}}{298.2^2} = 1.31$$

RATE CONSTANTS

Second Order, Figure A1

$$k = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.2} \times \frac{3}{9.7/60} = 93\ M^{-1}min^{-1}$$

First Order, Figure A2

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A3

SYSTEM: HYDRAZINE + 2,4-PENTANEDIONE

Initial Conditions: N_2H_4 0.2M, 2,4-PD 0.2M, T_o 15°C, K = 1.43 ▽

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$
0	0	0	0	0	0
1.0	1	0.61	0.022	0.178	0.124
2.1	2	1.02	0.038	0.162	0.233
3.2	3	1.60	0.059	0.141	0.421
4.3	4	2.14	0.079	0.121	0.657
5.4	5	2.56	0.095	0.105	0.903
6.6	6	2.84	0.105	0.095	1.112
7.8	7	3.09	0.114	0.084	1.37
9.0	8	3.29	0.122	0.078	1.56
10.2	9	3.46	0.128	0.072	1.78
11.4	10	3.62	0.134	0.066	2.04
13.8	12	3.87	0.143	0.057	2.52
16.3	14	4.05	0.150	0.050	3.00
18.8	16	4.19	0.155	0.045	3.45
21.3	18	4.33	0.160	0.040	4.02
23.8	20	4.45	0.165	0.035	4.69
28.9	24	4.61	0.171	0.029	5.85
34.1	28	4.74	0.175	0.025	7.17
39.2	32	4.85	0.180	0.020	8.79
44.4	36	4.92	0.182	0.018	10.29
∞	∞	5.40	0.200	0	∞

$$K = \frac{\frac{5.4}{0.2} \times \frac{8770}{1.986}}{288.2^2} = 1.43$$

RATE CONSTANTS

Second Order, Figure A1

$$k_{15} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.2} \times \frac{0.3}{15.5/60} = 58\ M^{-1}min^{-1}$$

$$k_{25} = k_{15}\ exp\ \frac{T_1-T_2}{T_1T_2}\frac{E}{R} = 58\ exp\ \frac{10x8770}{288.2x298.2x1.986} = 97\ M^{-1}min^{-1}$$

First Order, Figure A2

$$k_{15} = \frac{2.303}{t}\ log\ \frac{a}{a-x}$$ Curved

KINETIC DATA A4

SYSTEM: HYDRAZINE + 2,4-PENTANEDIONE

Initial Conditions: N_2H_4 0.1M, 2,4-PD 0.2M, T_o 25°C, K = 1.34 ⊙

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0	0.2000	0.1000	0
1.0	1	0.435	0.0161	0.1839	0.0839	+0.039
2.1	2	0.906	0.0336	0.1664	0.0664	0.099
3.1	3	1.213	0.0450	0.1550	0.0550	0.150
4.2	4	1.436	0.0532	0.1468	0.0468	0.194
5.3	5	1.612	0.0597	0.1403	0.0403	0.214
6.4	6	1.777	0.0659	0.1341	0.0341	0.294
7.5	7	1.890	0.0700	0.1300	0.0300	0.350
8.6	8	1.993	0.0738	0.1262	0.0262	0.382
10.8	10	2.15	0.0797	0.1203	0.0203	0.472
13.1	12	2.27	0.0840	0.1160	0.0160	0.559
15.3	14	2.37	0.0877	0.1123	0.0123	0.660
19.9	18	2.49	0.0922	0.1078	0.0078	0.849
24.4	22	2.57	0.0952	0.1048	0.0048	1.037
∞	∞	2.70	0.0000	0.1000	0	∞

$$K = \frac{\frac{2.7}{0.1} \times \frac{8770}{1.986}}{298.2^2} = 1.34$$

RATE CONSTANTS

Second Order, Figure A1

$$k_{25} = \frac{2.303}{(a-b)t} \cdot \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{0.1} \times \frac{0.915}{20/60} = 63\ M^{-1}min^{-1}$$

First Order, Figure A2

$$k_{25} = \frac{2.303}{t} \log \frac{b}{b-x}$$ Curved

KINETIC DATA A5

SYSTEM: HYDRAZINE + 2,4-PENTANEDIONE

Initial Conditions: N_2H_4 0.2M, 2,4-PD 0.1M, T_o 25°C, K = 1.24 ⊡

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0	0.1000	0.2000	0
1.0	1	0.127	0.0161	0.0839	0.1839	-0.011
2.0	2	0.452	0.0336	0.0664	0.1664	-0.045
3.1	3	0.922	0.0450	0.0550	0.1550	-0.111
4.1	4	1.250	0.0532	0.0468	0.1468	-0.176
5.2	5	1.487	0.0597	0.0403	0.1403	-0.237
6.3	6	1.667	0.0659	0.0341	0.1341	-0.300
7.4	7	1.821	0.0700	0.0300	0.1300	-0.371
8.5	8	1.930	0.0738	0.0262	0.1262	-0.428
10.7	10	2.120	0.0797	0.0203	0.1203	-0.574
13.0	12	2.240	0.0840	0.0160	0.1160	-0.722
15.2	14	2.315	0.0877	0.0123	0.1123	-0.895
19.8	18	2.40	0.0922	0.0078	0.1078	-1.113
24.3	22	2.46	0.0952	0.0048	0.1048	-1.311
∞	∞	2.50	0.1000	0.0000	0.1000	∞

$$K = \frac{\frac{2.5}{0.1} \times \frac{8770}{1.986}}{298.2^2} = 1.24$$

RATE CONSTANTS

Second Order, Figure A1

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{-0.1} \times \frac{(-0.795)}{14/60} = 79\ M^{-1}min^{-1}$$

First Order, Figure A2

$$k_{25} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A6

SYSTEM: HYDRAZINE + 2,4-PENTANEDIONE IN 3% GEL

Initial Conditions: N_2H_4 0.2M, 2,4-PD 0.2M, T_o 17°C, K = 1.63 ⊙

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$
0	0	0	0	0	0
1.10	1	1.84	0.059	0.1410	0.419
2.25	2	2.66	0.086	0.1140	0.755
4.64	4	3.40	0.1098	0.0902	1.218
7.11	6	4.00	0.1290	0.0710	1.818
9.63	8	4.41	0.1423	0.0577	2.47
12.20	10	4.74	0.1526	0.0474	3.22
14.80	12	4.98	0.1608	0.0392	4.10
20.10	16	5.32	0.1719	0.0281	6.13
25.45	20	5.58	0.1790	0.0210	8.54
30.96	24	5.71	0.1844	0.0156	11.82
36.40	28	5.81	0.1876	0.0124	15.13
∞	∞	6.2	0.2000	0.0000	∞

$$K = \frac{\frac{6.2}{0.2} \times \frac{8770}{1.986}}{(290.2)^2} = 1.63$$

RATE CONSTANTS

Second Order, Figure A1

$$k_{17} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.2} \times \frac{7}{27.5/60} = 76\ M^{-1}min^{-1}$$

$$k_{25} = k_{17} \exp\left(\frac{T_1-T_2}{T_1T_2}\right)\frac{E}{R} = 76 \exp\frac{10x8770}{290.2x298.2x1.986} = 116\ M^{-1}min^{-1}$$

First Order, Figure A2

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$ Curved

KINETIC DATA A7

SYSTEM: UDMH + 2,4-PENTANEDIONE

Initial Conditions: UDMH 0.8M, 2,4-PD 0.8M, T_o 27.2°C, $K = \frac{103.8}{300.4+\Delta T}$ △

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$	a-0.5x	$\log \frac{(a-0.5x)}{(a-x)}$
0	0	0	0	0.8	0	0	0
0.26	0.25	1.0	0.1	0.7	0.14	0.75	+0.031
0.53	0.5	1.8	0.18	0.62	0.29	0.71	0.059
0.80	0.75	2.5	0.25	0.55	0.46	0.67	0.086
1.08	1.0	3.0	0.30	0.50	0.60	0.65	0.114
1.36	1.25	3.6	0.36	0.44	0.82	0.62	0.149
1.65	1.5	3.9	0.39	0.41	0.95	0.60	0.166
1.94	1.75	4.5	0.45	0.35	1.29	0.57	0.212
2.23	2	4.8	0.48	0.32	1.50	0.56	0.243
3.45	3	5.8	0.58	0.22	2.64	0.51	0.365
4.69	4	6.3	0.63	0.17	3.70	0.48	0.451
5.95	5	6.8	0.68	0.12	5.66	0.46	0.584
7.23	6	7.2	0.72	0.08	9.00	0.44	0.741
∞	∞	8.0	0.80	0	∞	0.40	∞

$$K = \frac{\frac{8}{0.8} \times \frac{6200}{1.986}}{300.4\ (300.4+\Delta T)} = \frac{103.8}{(300.4+\Delta T)}$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A3

$$k_{27.2} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.8} \times \frac{3.95}{6} = 0.82_3\ M^{-1}min^{-1}$$

$$k_{25} = k_{27.2} \exp \frac{-2.2 \times \frac{6200}{1.986}}{298.2 \times 300.4} = 0.823/1.079 = 0.76\ M^{-1}min^{-1}\ \text{(curved)?}$$

Second Order, 2:1 stoichiometry, Figure A5

$$k_{27.2} = \frac{1}{(a-.5b)t} \log \frac{b}{a}\frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.4} \times \frac{773}{7.5} = 0.59_3\ M^{-1}min^{-1}$$

$$k_{25} = k_{27.2} \exp \frac{-2.2 \times \frac{6200}{1.986}}{298.2 \times 300.4} = 0.593/1.079 = 0.55\ M^{-1}min^{-1}$$

First Order, Figure A7

$$k_{27.5} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A8

SYSTEM: UDMH + 2,4-PENTANEDIONE

Initial Conditions: UDMH 0.8M, 2,4-PD 0.8M, T_o 17.2°C, $K = \frac{170.4}{(290.4+\Delta T)}$ ▽

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$	a-0.5x	$\log \frac{(a-0.5x)}{(a-x)}$
0	0	0	0	0.80	0	0	0
0.52	0.5	1.2	0.12	0.68	0.18	0.74	+0.037
1.06	1.0	2.2	0.22	0.58	0.38	0.69	0.068
1.62	1.5	3.0	0.30	0.50	0.60	0.65	0.114
2.19	2.0	3.7	0.37	0.43	0.86	0.61	0.153
3.38	3.0	4.9	0.49	0.31	1.58	0.55	0.249
4.50	4.0	5.5	0.55	0.25	2.20	0.52	0.318
5.74	5.0	6.0	0.60	0.20	3.00	0.50	0.398
7.01	6.0	6.7	0.67	0.13	5.15	0.47	0.559
8.29	7.0	7.0	0.70	0.10	7.00	0.45	0.653
9.59	8.0	7.3	0.73	0.07	10.4	0.43	0.779
10.91	9.0	7.8	0.78	0.02	39.0	0.41	1.312
∞	∞	8.0	0.80	0	∞	0.40	∞

$$K = \frac{\frac{8}{0.8} \times \frac{6200}{1.986}}{290.4\ (290.4+\Delta T)} = \frac{107.4}{(290.4+\Delta T)}$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A3

$$k_{17.2} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.8} \times \frac{3.2}{6} = 0.66_7\ M^{-1}min^{-1}$$

$$k_{25} = k_{17.2} \exp \frac{7.8 \times \frac{6200}{1.986}}{290.4x298.2} = 0.66_7 \times 1.325 = 0.88\ M^{-1}min^{-1}\ \text{(curved)?}$$

Second Order, 2:1 stoichiometry, Figure A5

$$k_{17.2} = \frac{1}{(a-.5b)t} \log \frac{b}{a}\frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.4} \times \frac{.545}{7.5} = 0.41_9\ M^{-1}min^{-1}$$

$$k_{25} = k_{17.2} \exp \frac{7.8 \times \frac{6200}{1.982}}{290.4x298.2} = 0.419 \times 1.325 = 0.55\ M^{-1}min^{-1}$$

First Order, Figure A7

$$k_{17.2} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A9

SYSTEM: UDMH + 2,4-PENTANEDIONE

Initial Conditions: UDMH 0.8M, 2,4-PD 0.4M, T_o 26.2°C, K = 0.402

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	$\frac{x}{a-x}=\frac{2x}{b-2x}$
0	0	0	0	0.400	0.800	0	0
1.07	1	1.8	0.166	0.234	0.634	-0.132	0.71
2.16	2	2.7	0.235	0.165	0.565	-0.234	1.42
3.29	3	3.3	0.288	0.112	0.512	-0.359	2.57
4.42	4	3.6	0.314	0.086	0.486	-0.452	3.65
5.57	5	3.9	0.340	0.060	0.460	-0.583	5.67
6.73	6	4.2	0.366	0.034	0.434	-0.804	10.77
7.90	7	4.4	0.383	0.017	0.417	-1.251	32.7
∞	∞	4.6	0.400	0.000	0.400	∞	∞

$$K = \frac{\frac{4.6}{0.4} \times \frac{6200}{1.986}}{299.4^2} = 0.402$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A4

$$k_{26.2} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{-0.4} \times \frac{(-.773)}{7.5} = 0.59_4 \ M^{-1}min^{-1}$$

$$k_{25} = k_{26.2} \exp \frac{-1.2 \times \frac{6200}{1.986}}{299.4x298.2} = \frac{0.594}{1.042} = 0.57 \ M^{-1}min^{-1}$$

Second Order, 2:1 stoichiometry, Figure A6

$$k_{26.2} = \frac{1}{bt}\frac{2x}{b-2x} = \frac{1}{2at}\frac{x}{(a-x)} \quad \text{Curved}$$

First Order, Figure A8

$$k_{26.2} = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{Curved}$$

KINETIC DATA A10

SYSTEM: UDMH + 2,4-PENTANEDIONE[a]

Initial Conditions: UDMH 0.4M, 2,4-PD 0.8M, T_o 25.0°C, K = 0.345 ⊙

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	a-0.5x (M)	$\log \frac{b}{a}\frac{(a-0.5x)}{(b-x)}$
0	0	0	0	0.800	0.400	0	0.800	0
1.04	1	1.0	0.103	0.697	0.297	+0.070	0.748	+0.100
2.11	2	2.0	0.205	0.595	0.195	0.184	0.697	0.252
3.20	3	2.3	0.236	0.564	0.164	0.236	0.682	0.318
4.30	4	2.6	0.267	0.533	0.133	0.303	0.666	0.399
5.41	5	2.8	0.287	0.513	0.113	0.356	0.656	0.463
6.52	6	3.1	0.318	0.482	0.082	0.469	0.641	0.592
7.65	7	3.4	0.349	0.451	0.051	0.647	0.625	0.788
8.78	8	3.6	0.369	0.431	0.031	0.843	0.615	0.997
9.92	9	3.7	0.380	0.420	0.020	1.022	0.610	1.184
∞	∞	3.9	0.400	0.400	0.000	∞	0.600	∞

$$K = \frac{\frac{3.9}{.4} \times \frac{6200}{1.986}}{298.2^2} = 0.345$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A4

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{.4} \times \frac{.543}{7.5} = 0.42\ M^{-1}min^{-1}$$

Second Order, 2:1 stoichiometry, Figure A6

$$k_{25} = \frac{2.303}{(a-.5b)t} \log \frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.6} \times \frac{0.766}{7.5} = 0.39\ M^{-1}min^{-1}\ ^{(b)}$$

First Order, Figure A8

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

Note: (a) First Run. (b) Averaged with second run.

KINETIC DATA A11

SYSTEM: UDMH + 2,4-PENTANEDIONE[a]

Initial Conditions: UDMH 0.4M, 2,4-PD 0.8M, T_o 25°C, K = 0.395 ①

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	a-0.5x (M)	$\log \frac{b}{a}\frac{(a-0.5x)}{(b-x)}$
0	0	0	0	0	0.400	0	0	0
0.51	0.5	0.36	0.032	0.768	0.368	+0.019	0.784	+0.028
1.01	1.0	0.76	0.068	0.732	0.332	0.043	0.766	0.063
1.54	1.5	1.11	0.099	0.701	0.301	0.067	0.750	0.095
2.07	2.0	1.62	0.144	0.656	0.256	0.109	0.728	0.153
2.61	2.5	2.12	0.189	0.611	0.211	0.161	0.705	0.222
3.16	3.0	2.52	0.224	0.576	0.176	0.214	0.688	0.292
3.71	3.5	2.79	0.248	0.552	0.152	0.258	0.676	0.348
4.27	4.0	3.06	0.272	0.528	0.128	0.315	0.664	0.414
4.73	4.5	3.29	0.293	0.507	0.107	0.375	0.654	0.485
5.30	5.0	3.54	0.315	0.485	0.085	0.455	0.642	0.578
5.87	5.5	3.74	0.333	0.467	0.067	0.542	0.633	0.675
6.44	6.0	4.01	0.357	0.443	0.043	0.699	0.621	0.859
7.03	6.5	4.15	0.369	0.431	0.031	0.843	0.615	0.997
7.61	7.0	4.31	0.384	0.416	0.016	1.115	0.608	1.279
∞	∞	4.50	0.400	0.400	0.000	∞	0.600	∞

$$K = \frac{\frac{4.5}{.4} \times \frac{6200}{1.986}}{298.2^2} = 0.395$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A4

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} \quad \text{Curved}$$

Second Order, 2:1 stoichiometry, Figure A6

$$k_{25} = \frac{2.303}{(a-0.5b)t} \log \frac{b}{a}\frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.6} \times \frac{.766}{7.5} = 0.39\ M^{-1}min^{-1}\ ^{(b)}$$

First Order, Figure A8

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{Curved}$$

Note: (a) Second run. (b) Average with first run.

KINETIC DATA A12

SYSTEM: UDMH + 2,4-PENTANEDIONE[(a)]

Initial Conditions: UDMH 0.4M, 2,4-PD 0.8M, T_o 25.0°C, K = 0.400 ⊖

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	a-0.5x (M)	$\log \frac{b}{a}\frac{(a-0.5x)}{(b-x)}$
0	0	0	0	0.800	0.400	0	0	0
0.51	0.5	0.43	0.038	0.762	0.362	+0.022	0.781	+0.034
1.03	1.0	0.85	0.075	0.725	0.325	0.047	0.762	0.070
1.55	1.5	1.23	0.109	0.691	0.291	0.074	0.745	0.107
2.09	2.0	1.55	0.137	0.663	0.263	0.110	0.731	0.144
2.62	2.5	1.80	0.159	0.641	0.241	0.124	0.720	0.174
3.17	3.0	2.06	0.183	0.617	0.217	0.153	0.708	0.212
3.72	3.5	2.29	0.203	0.597	0.197	0.180	0.698	0.247
4.27	4.0	2.48	0.220	0.580	0.180	0.207	0.690	0.283
4.83	4.5	2.66	0.237	0.563	0.163	0.236	0.681	0.321
5.39	5.0	2.82	0.250	0.550	0.150	0.257	0.675	0.352
6.52	6.0	3.08	0.272	0.528	0.128	0.314	0.664	0.414
7.67	7.0	3.31	0.293	0.507	0.107	0.374	0.653	0.485
8.82	8.0	3.48	0.308	0.492	0.092	0.428	0.646	0.546
9.98	9.0	3.64	0.321	0.479	0.079	0.481	0.639	0.607
11.05	10.0	3.75	0.332	0.468	0.068	0.536	0.634	0.668
13.39	12.0	3.85	0.340	0.460	0.060	0.583	0.630	0.720
15.74	14.0	3.99	0.353	0.447	0.047	0.678	0.623	0.822
∞	∞	4.55	0.400	0.400	0.000	∞	0.600	∞

$$K = \frac{\frac{4.55}{0.4} \times \frac{6200}{1.986}}{298.2^2} = 0.400$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A4

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{(0.4)} \times \frac{0.437}{9} = 0.28\ M^{-1}min^{-1}$$

Second Order, 2:1 stoichiometry, Figure A6

$$k_{25} = \frac{2.303}{(a-0.5b)t} \log \frac{b}{a}\frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.6} \times \frac{.586}{9} = 0.25\ M^{-1}min^{-1}$$

First Order, Figure A8

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

Note: (a) Third run.

KINETIC DATA A13

SYSTEM: UDMH + 2,4-PENTANEDIONE

Initial Conditions: UDMH 0.4M, 2,4-PD 0.4M, T_o 25°C, K = 0.360 ⊙

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$	a-0.5x (M)	$\log \frac{(a-0.5x)}{(a-x)}$
0	0	0	0	0.400	0	0	0
1.02	1	0.43	0.042	0.358	0.117	.379	+0.025
2.05	2	0.83	0.073	0.327	0.223	.358	0.040
3.09	3	1.20	0.106	0.294	0.361	.340	0.063
4.15	4	1.51	0.133	0.267	0.498	.333	0.096
5.21	5	1.77	0.156	0.244	0.640	.324	0.123
6.29	6	1.97	0.174	0.226	0.770	.313	0.141
8.47	8	2.35	0.208	0.192	1.083	.294	0.185
10.66	10	2.64	0.233	0.167	1.395	.283	0.229
12.88	12	2.87	0.254	0.146	1.738	.273	0.272
15.11	14	3.04	0.268	0.132	2.03	.266	0.305
17.35	16	3.18	0.281	0.119	2.36	.259	0.347
21.88	20	3.40	0.301	0.099	3.04	.249	0.401
27.57	25	3.60	0.318	0.082	3.88	.241	0.469
33.30	30	3.77	0.333	0.067	4.97	.233	0.542
39.05	35	3.85	0.340	0.060	5.67	.230	0.583
∞	∞	4.10	0.400	0.000	∞	.200	∞

$$K = \frac{\frac{4.10}{0.4} \times \frac{6200}{1.986}}{298.2^2} = 0.360$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A3

$$k_{25} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.4} \times \frac{4.4}{30} = 0.37\ M^{-1}min^{-1}$$

Second Order, 2:1 stoichiometry, Figure A5

$$k_{25} = \frac{2.303}{(a-0.5b)t} \log \frac{b}{a}\frac{(a-0.5x)}{(b-x)} = \frac{2.303}{0.2} \times \frac{61}{30} = 0.234\ M^{-1}min^{-1}$$

First Order, Figure A7

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A14

SYSTEM: HYDRAZINE + FORMALDEHYDE

Initial Conditions: N_2H_4 0.2M, HCHO 0.2M, T_o 25.0°C, K = 0.748 △

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$	2b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-0.5x)}$
0	0	0	0	0.200	0	0.200	0
2.02	2	0.124	0.016	0.184	0.087	0.192	-0.017
4.06	4	0.214	0.024	0.176	0.136	0.188	-0.028
6.12	6	0.320	0.040	0.160	0.250	0.180	-0.051
8.20	8	0.445	0.056	0.144	0.389	0.172	-0.077
10.31	10	0.570	0.071	0.129	0.550	0.165	-0.105
14.61	14	0.765	0.096	0.104	0.924	0.152	-0.165
18.97	18	0.925	0.116	0.084	1.382	0.142	-0.227
23.39	22	1.068	0.133	0.067	1.97	0.134	-0.299
27.85	26	1.176	0.147	0.053	2.78	0.127	-0.377
32.35	30	1.263	0.158	0.042	3.76	0.122	-0.459
36.87	34	1.317	0.164	0.036	4.55	0.118	-0.515
41.41	38	1.370	0.171	0.029	5.90	0.115	-0.596
45.98	42	1.423	0.178	0.022	8.10	0.111	-0.703
50.56	46	1.460	0.182	0.018	10.10	0.109	-0.782
55.15	50	1.468	0.184	0.016	11.5	0.108	-0.829
∞	∞	1.600	0.200	0.000	∞	0.100	∞

$$K = \frac{\frac{1.60}{0.2} \times \frac{16{,}500}{1.986}}{298.2^2} = 0.748$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A9

$$k_{25} = \frac{1}{at}\frac{x}{a-x} \quad \text{Curved}$$

Second Order, 1:2 stoichiometry, Figure A10

$$k_{25} = \frac{2.303}{(0.5a-b)t} \log \frac{b\,(a-x)}{a(b-0.5x)} = \frac{2.303}{-0.1} \times \frac{(-0.5)}{33/60} = 21\ M^{-1}min^{-1}$$

First Order, Figure A11

$$k_{25} = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40/60} \log \frac{0.208}{0.0315} = 2.8\ min^{-1}$$

KINETIC DATA A15

SYSTEM: HYDRAZINE + FORMALDEHYDE

Initial Conditions: N_2H_4 0.2M, HCHO 0.2M, T_o 15°C, K = 1.000 ▽

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$	b-0.5x (M)	$\log \frac{b}{a} \frac{(a-x)}{(b-0.5x)}$
0	0	0	0	0.200	0	0.400	0
12.44	12	0.35	0.035	0.165	0.212	0.182	-0.043
25.32	24	0.69	0.069	0.131	0.526	0.166	-0.102
38.55	36	0.96	0.096	0.104	0.923	0.152	-0.164
52.07	48	1.20	0.120	0.080	1.50	0.140	-0.244
65.85	60	1.38	0.138	0.062	2.13	0.131	-0.325
79.85	72	1.53	0.153	0.047	3.26	0.124	-0.419
94.01	84	1.64	0.164	0.036	4.55	0.138	-0.516
108.22	96	1.67	0.167	0.033	5.06	0.117	-0.548
122.54	108	1.75	0.175	0.025	7.00	0.113	-0.652
136.91	120	1.79	0.179	0.021	8.53	0.111	-0.721
∞	∞	2.00	0.200	0	∞	0.200	∞

$$K = \frac{\frac{2.00}{0.2} \times \frac{16,500}{1.986}}{288.2^2} = 1.000$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A9

$$k_{15} = \frac{1}{at} \frac{x}{a-x} \quad \text{Curved}$$

Second Order, 1:2 stoichiometry, Figure A10

$$k_{15} = \frac{2.303}{(0.5a-b)t} \log \frac{b}{a} \frac{(a-x)}{(b-0.5x)} = \frac{2.303}{-0.1} \times \frac{(-0.3)}{63.5/60} = 6.5_3 \ M^{-1}min^{-1}$$

$$k_{25} = k_{15} \exp \frac{298.2-288.2}{298.2x288.2} \times \frac{16,500}{1.986} = 16.1 \ M^{-1}min^{-1}$$

First Order, Figure A11

$$k_{15} = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{90/60} \log \frac{0.205}{0.038} = 1.122 \ min^{-1}$$

$$k_{25} = k_{15} \exp \frac{298.2-288.2}{298.2x288.2} \times \frac{16,500}{1.986} = 3.0 \ min^{-1}$$

KINETIC DATA A16

SYSTEM: HYDRAZINE + FORMALDEHYDE

Initial Conditions: N_2H_4 0.4M, HCHO 0.2M, T_o 25°C, K = 0.763

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	b-0.5x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-0.5x)}$
0	0	0	0	0.200	0.400	0.00	0.400	0
2.03	2	0.16	0.020	0.180	0.380	-0.024	0.390	-0.035
4.08	4	0.27	0.033	0.167	0.367	-0.041	0.384	-0.060
6.15	6	0.36	0.044	0.156	0.356	-0.058	0.378	-0.084
8.24	8	0.47	0.058	0.142	0.342	-0.081	0.371	-0.116
10.35	10	0.55	0.067	0.133	0.333	-0.097	0.366	-0.139
12.48	12	0.67	0.082	0.118	0.318	-0.129	0.359	-0.183
14.63	14	0.76	0.093	0.107	0.307	-0.158	0.353	-0.219
16.80	16	0.86	0.104	0.096	0.296	-0.188	0.348	-0.259
18.98	18	0.91	0.111	0.089	0.289	-0.210	0.344	-0.287
22.17	20	0.97	0.118	0.082	0.282	-0.235	0.341	-0.318
26.72	25	1.11	0.136	0.064	0.264	-0.314	0.332	-0.414
32.34	30	1.26	0.153	0.047	0.247	-0.420	0.323	-0.537
38.00	35	1.33	0.162	0.038	0.238	-0.495	0.319	-0.623
43.71	40	1.42	0.173	0.027	0.227	-0.624	0.313	-0.764
49.44	45	1.46	0.178	0.022	0.222	-0.703	0.311	-0.849
∞	∞	1.64	0.200	0	0.200	∞	0.300	∞

$$K = \frac{\frac{1.64}{0.2} \times \frac{16,500}{1.986}}{298.2^2} = 0.763$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A9

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{-0.2} \times \frac{(-0.6)}{57/60} = 17.3\ M^{-1}min^{-1}$$

Second Order, 1:2 stoichiometry, Figure A10

$$k_{25} = \frac{2.303}{(0.5a-b)t} \times \log \frac{b}{a}\frac{(a-x)}{(b-0.5x)} = \frac{2.303}{-0.3} \times \frac{(-0.8)}{50.5/60} = 7.3\ M^{-1}min^{-1}$$

First Order, Figure A11

$$k_{25} = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{45/60} \log \frac{0.196}{0.0256} = 2.7\ min^{-1}$$

KINETIC DATA A17

SYSTEM: HYDRAZINE + FORMALDEHYDE

Initial Conditions: N_2H_4 0.2M, HCHO 0.4M, T_o 25°C, K = 1.600 ⊙

Corr. Time (sec)	Time (sec)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$	$\frac{2x}{a-x}$
0	0	0	0	0	0	0	0
2.05	2	0.26	0.015	0.385	0.185	+0.018	0.081
4.15	4	0.51	0.030	0.370	0.170	0.037	0.176
6.30	6	0.79	0.046	0.354	0.156	0.055	0.295
8.50	8	1.04	0.061	0.339	0.139	0.086	0.439
10.75	10	1.26	0.074	0.326	0.126	0.112	0.588
13.05	12	1.48	0.086	0.314	0.114	0.139	0.755
17.81	16	1.86	0.108	0.292	0.092	0.200	1.175
22.70	20	2.05	0.126	0.274	0.074	0.267	1.704
27.69	24	2.37	0.139	0.261	0.061	0.330	2.28
32.75	28	2.52	0.147	0.253	0.053	0.377	2.78
37.89	32	2.69	0.157	0.243	0.043	0.451	3.66
43.08	36	2.77	0.163	0.237	0.037	0.505	4.30
48.32	40	2.88	0.168	0.232	0.032	0.559	5.25
56.23	46	2.96	0.172	0.228	0.028	0.609	6.14
64.20	52	3.05	0.177	0.223	0.023	0.686	7.80
72.22	58	3.10	0.181	0.219	0.019	0.760	9.53
∞	∞	3.43	0.200	0.200	0.000	∞	∞

$$K = \frac{\frac{3.43}{0.2} \times \frac{16,500}{1.986}}{298.6^2} = 1.600$$

RATE CONSTANTS

Second Order, 1:1 stoichiometry, Figure A9

$$k_{25} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{0.2} \times \frac{0.5}{57/60} = 7.3\ M^{-1}min^{-1}$$

Second Order, 1:2 stoichiometry, Figure A10

$$k_{25} = \frac{1}{at}\frac{2x}{a-x}$$ Curved Note: b = 0.5a is substituted into the differential eqn.

First Order, Figure A11

$$k_{25} = \frac{2.303}{t} \log \frac{b}{b-x} = \frac{2.303}{56/60} \times 1.00 = 2.5\ min^{-1}$$ 1st step

$$k_{25} = \frac{2.303}{t} \log \frac{b}{b-x} = \frac{2.303}{90/60} \times .962 = 1.29\ min^{-1}$$ 2nd step

KINETIC DATA A18

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH 0.8M, HCHO 0.8M, T_o 27°C, $K = \frac{608}{300.2+\Delta T}$ △

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$
0	0	0	0	0.800	0
1.10	1	0.9	0.048	0.752	0.064
2.49	2	3.1	0.165	0.635	0.260
4.26	3	5.4	0.285	0.515	0.554
6.40	4	7.3	0.386	0.414	0.934
8.98	5	9.1	0.482	0.318	1.515
11.83	6	10.0	0.538	0.262	2.055
14.91	7	10.9	0.577	0.223	2.50
18.22	8	11.6	0.614	0.186	3.30
21.78	9	12.3	0.652	0.148	4.40
25.62	10	13.1	0.694	0.106	6.55
∞	∞	15.1	0.800	0.000	∞

$$K = \frac{\frac{15.1}{0.8} \times \frac{19,200}{1.986}}{300.2(300.2+T)} = \frac{608}{300.2+\Delta T}$$

RATE CONSTANTS

Second Order, Figure A12

$$k_{27} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{.8} \times \frac{0.566}{30} = 0.236\ M^{-1}min^{-1}$$

$$k_{25} = k_{27} \times \exp \frac{2 \times \frac{19,200}{1.986}}{300.2 \times 298.2} = 0.236 \times 0.804 = 0.19\ M^{-1}min^{-1}$$

First Order, Figure A14

$$k_{27} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A19

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH 0.8M, HCHO 0.8M, T_o 17°C, $K = \frac{639}{(290.2+\Delta T)}$ ▽

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	$\frac{x}{a-x}$
0	0	0	0	0.800	0.000
2.12	2	0.5	0.026	0.774	0.034
4.47	4	1.4	0.074	0.726	0.102
7.34	6	3.1	0.165	0.635	0.259
10.88	8	5.0	0.264	0.536	0.492
15.08	10	6.3	0.333	0.467	0.713
19.88	12	7.7	0.408	0.392	1.041
25.48	14	9.1	0.482	0.318	1.513
31.52	16	9.8	0.518	0.282	1.835
37.88	18	10.3	0.545	0.255	2.14
44.84	20	11.1	0.588	0.212	2.77
52.20	22	11.6	0.615	0.185	3.33
59.96	24	12.1	0.642	0.158	4.06
68.06	26	12.5	0.662	0.138	4.80
∞	∞	15.1	0.800	0.000	∞

$$K = \frac{\frac{15.1}{0.8} \times \frac{19,200}{1.986}}{290.2(290.2+\Delta T)} = \frac{639}{(290.2+\Delta T)}$$

RATE CONSTANTS

Second Order, Figure A12

$$k_{17} = \frac{1}{at}\frac{x}{a-x} = \frac{1}{0.8} \times \frac{4}{60} = 0.083_4 \ M^{-1}min^{-1}$$

$$k_{25} = k_{17} \exp \frac{8 \times \frac{19,200}{1.986}}{290.2 \times 298.2} = 0.0083_4 \times 2.44 = 0.20 \ M^{-1}min^{-1}$$

First Order, Figure A14

$$k_{17} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved.

KINETIC DATA A20

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH 0.8M, HCHO 0.4M, T_o 26.5°C, $K = \frac{678}{(299.7+\Delta T)}$ □

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0	0.400	0.800	0
2.2	2	0.73	0.035	0.365	0.765	-0.020
4.5	4	1.28	0.061	0.339	0.739	-0.028
6.9	6	1.82	0.087	0.313	0.713	-0.057
9.4	8	2.34	0.112	0.288	0.688	-0.077
12.1	10	2.73	0.131	0.269	0.669	-0.094
18.0	14	3.55	0.169	0.231	0.631	-0.135
24.2	18	4.19	0.200	0.200	0.600	-0.176
31.0	22	4.77	0.237	0.163	0.563	-0.238
41.8	28	5.50	0.263	0.137	0.537	-0.292
53.2	34	6.14	0.293	0.107	0.507	-0.376
65.2	40	6.55	0.313	0.087	0.487	-0.452
77.8	46	7.00	0.334	0.066	0.466	-0.548
95.3	54	7.44	0.355	0.045	0.445	-0.694
113.2	62	7.70	0.367	0.033	0.433	-0.817
131.7	70	7.97	0.381	0.019	0.419	-1.042
-	-	8.40	0.400	0.000	0.400	-

$$K = \frac{\frac{8.4}{0.4} \times \frac{19,200}{1.986}}{299.5(299.5+\Delta T)} = \frac{678}{(299.5+\Delta T)}$$

RATE CONSTANTS

Second Order, 1:1, Figure A13

$$k_{26.5} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{-0.4} \times \frac{(-0.596)}{80} = 0.0430 \ M^{-1}min^{-1}$$

$$k_{25} = k_{26.5} \exp \frac{-1.5 \times \frac{19,200}{1.986}}{299.7 \times 298.2} = 0.043 \times 0.852 = 0.037 \ M^{-1}min^{-1}$$

First Order, Figure A14

$$k_{26.5} = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{60} \log \frac{0.400}{0.0715} = 0.029 \ min^{-1}$$

$$k_{25} = k_{26.5} \exp \frac{-1.5}{299.7 \times 298.2} \times \frac{19,200}{1.986} = 0.024 \ min^{-1}$$

KINETIC DATA A21

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH 0.8M, HCHO 1.6M, T_o = 27.0°C, $K = \frac{966}{300.2+\Delta T}$ ◇

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0.000	1.600	0.800	0.000
0.54	0.5	0.95	0.032	1.568	0.768	+0.009
1.20	1.0	2.6	0.088	1.512	0.712	0.025
2.04	1.5	4.9	0.165	1.435	0.635	0.053
3.15	2.0	7.6	0.253	1.347	0.547	0.090
4.61	2.5	10.4	0.347	1.253	0.453	0.142
6.51	3.0	13.1	0.435	1.165	0.365	0.213
8.86	3.5	15.2	0.506	1.094	0.294	0.270
11.65	4.0	16.9	0.565	1.035	0.235	0.342
18.47	5	19.1	0.635	0.965	0.165	0.466
26.27	6	20.5	0.682	0.918	0.118	0.612
34.59	7	21.2	0.705	0.895	0.095	0.673
43.47	8	21.9	0.729	0.871	0.071	0.788
∞	∞	24.0	0.800	0.800	0.000	∞

$$K = \frac{\frac{24}{0.8} \times \frac{19,200}{1.986}}{300.2(300.2+\Delta T)} = \frac{966}{(300.2+\Delta T)}$$

RATE CONSTANTS

Second Order, Figure A13

$$k_{27} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{0.8} \times \frac{0.575}{20} = 0.083_0 \ M^{-1}min^{-1}$$

$$k_{25} = k_{27} \exp \frac{-2 \times \frac{19,200}{1.986}}{300.2 \times 298.2} = 0.083_0 \times 0.805 = 0.067 \ M^{-1}min^{-1}$$

First Order, Figure A15

$$k_{27} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A22

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH = 0.4M, HCHO = 0.8M, T_o 24°C, $K = \frac{1016}{(297.2+\Delta T)}$ ⊙

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0	0.800	0.400	0
1.02	1	0.2	0.006	0.794	0.394	+0.010
2.18	2	1.3	0.042	0.738	0.338	0.038
3.49	3	2.6	0.083	0.717	0.317	0.054
5.03	4	4.0	0.128	0.672	0.272	0.093
6.77	5	5.2	0.166	0.634	0.234	0.131
8.77	6	6.5	0.208	0.592	0.192	0.188
11.00	7	7.7	0.246	0.554	0.154	0.255
13.48	8	8.5	0.272	0.528	0.128	0.314
16.14	9	9.2	0.294	0.506	0.106	0.379
18.96	10	9.8	0.313	0.487	0.087	0.447
25.20	12	10.8	0.345	0.455	0.055	0.616
31.76	14	11.3	0.361	0.439	0.039	0.750
38.58	16	11.8	0.373	0.427	0.027	0.898
∞	∞	12.5	0.400	0.400	0.000	∞

$$K = \frac{\frac{12.5}{0.4} \times \frac{19,200}{1.986}}{297.2 \times (297.2+\Delta T)} = \frac{1016}{297.2+\Delta T}$$

RATE CONSTANTS

Second Order, Figure A13

$$k_{24} = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{0.4} \times \frac{0.735}{30} = 0.141\ M^{-1}min^{-1}$$

$$k_{25} = k_{24} \exp \frac{1.0 \times \frac{19,200}{1.986}}{297.2 \times 298.2} = 0.141 \times 1.115 = 0.16\ M^{-1}min^{-1}$$

First Order, Figure A15

$$k_{24} = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

KINETIC DATA A23

SYSTEM: UDMH + FORMALDEHYDE

Initial Conditions: UDMH 0.4M, HCHO 1.6M, T_o 25°C, $K = \frac{1402}{(298.2+T)}$ ⊖

Corr. Time (min)	Time (min)	ΔT (°C)	x (M)	a-x (M)	b-x (M)	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0	0	0	1.600	0.400	0.000
1.08	1	0.7	0.016	1.584	0.384	+0.014
2.35	2	2.2	0.051	1.549	0.349	0.045
3.88	3	4.0	0.092	1.508	0.308	0.088
5.77	4	6.0	0.138	1.462	0.262	0.146
8.05	5	7.8	0.180	1.420	0.220	0.208
10.77	6	9.5	0.219	1.381	0.181	0.281
17.63	8	11.8	0.273	1.327	0.127	0.417
25.51	10	13.2	0.304	1.296	0.096	0.529
33.95	12	14.0	0.321	1.279	0.079	0.606
43.15	16	15.2	0.351	1.249	0.049	0.804
53.55	20	15.8	0.365	1.235	0.035	0.946
74.99	24	16.3	0.377	1.223	0.023	1.125
97.39	28	16.7	0.385	1.215	0.015	1.353
∞	∞	17.3	0.400	1.200	0.000	∞

$$K = \frac{\frac{17.3}{0.4} \times \frac{19,200}{1.986}}{298.2(298.2+\Delta T)} = \frac{1402}{(298.2+\Delta T)}$$

RATE CONSTANTS

Second Order, Figure A13

$$k = \frac{2.303}{(a-b)t} \log \frac{b}{a}\frac{(a-x)}{(b-x)} = \frac{2.303}{1.2} \times \frac{0.740}{30} = 0.047\ M^{-1}min^{-1}$$

First Order, Figure A15

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$ Curved

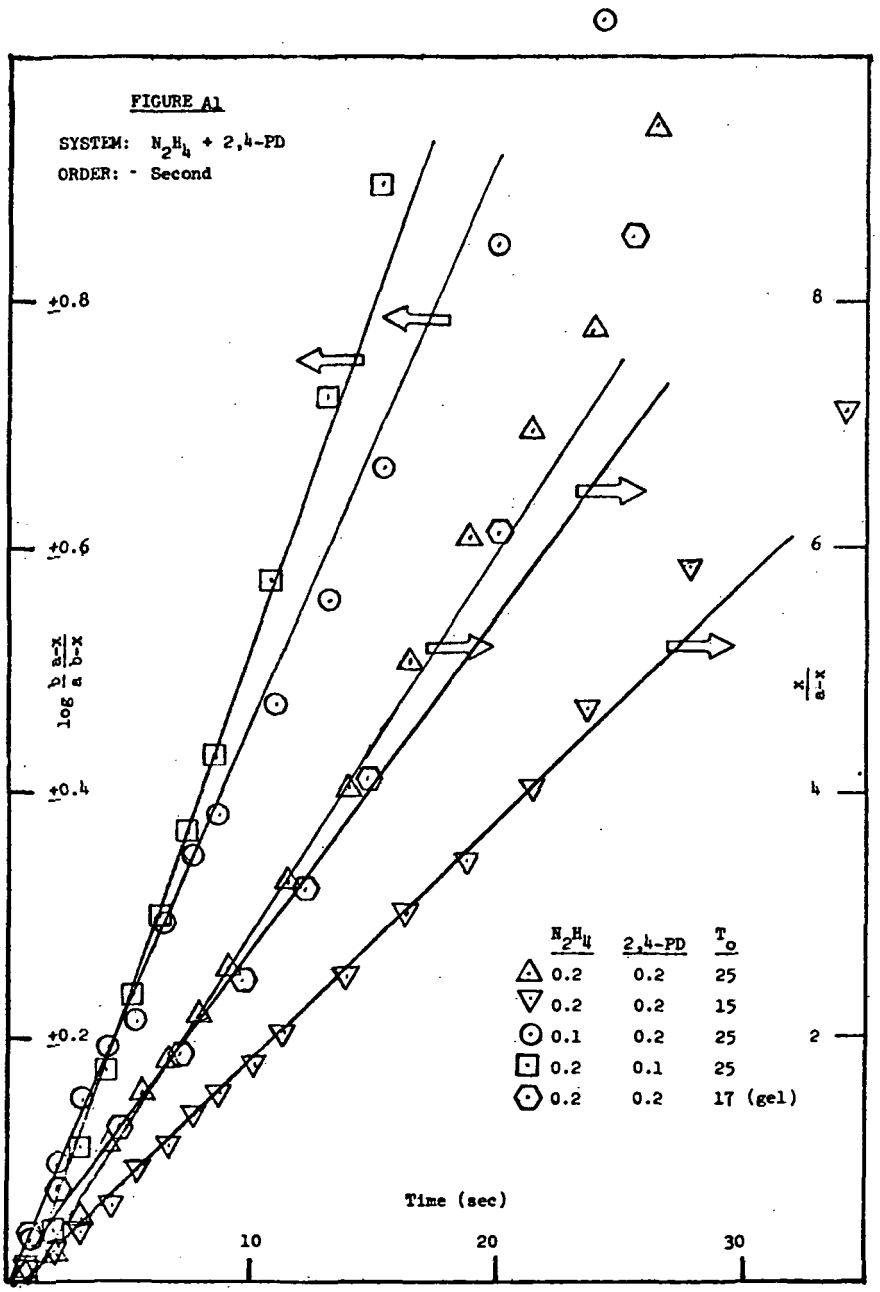


FIGURE A1
SYSTEM: N_2H_4 + 2,4-PD
ORDER: - Second
±0.8
±0.6
±0.4
±0.2
log a/b · b-x/a-x
8
6
4
2
x/a-x
Time (sec)
10
20
30
N_2H_4 2,4-PD T_o
0.2 0.2 25
0.2 0.2 15
0.1 0.2 25
0.2 0.1 25
0.2 0.2 17 (gel)

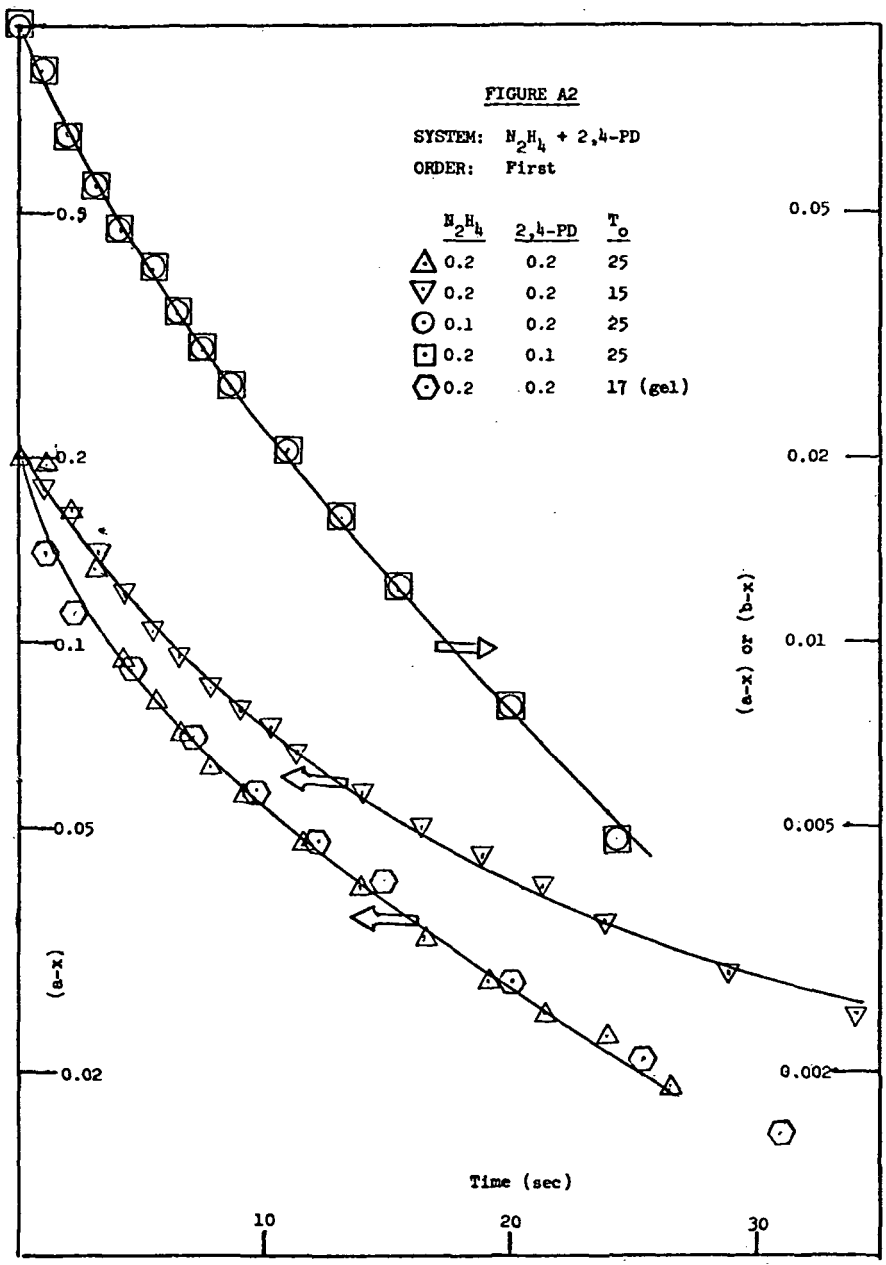
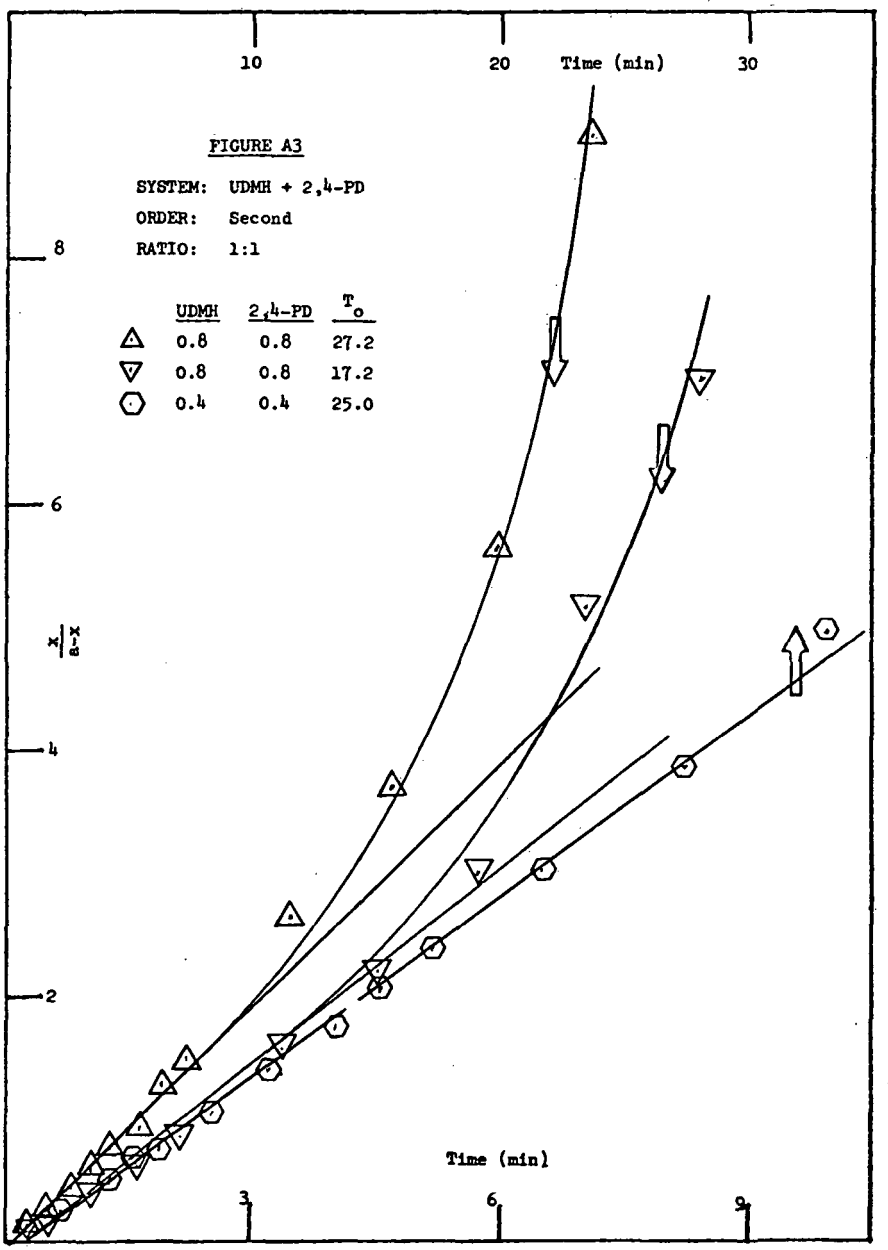


FIGURE A2
SYSTEM: N_2H_4 + 2,4-PD
ORDER: First
N_2H_4 2,4-PD T_o
0.2 0.2 25
0.2 0.2 15
0.1 0.2 25
0.2 0.1 25
0.2 0.2 17 (gel)
0.9
0.2
0.1
0.05
0.02
(a-x)
0.05
0.02
0.01
0.005
0.002
(a-x) or (b-x)
Time (sec)
10
20
30


10
20
Time (min)
30
FIGURE A3
SYSTEM: UDMH + 2,4-PD
ORDER: Second
RATIO: 1:1
UDMH 2,4-PD T_o
0.8 0.8 27.2
0.8 0.8 17.2
0.4 0.4 25.0
8
6
4
2
$x/a-x$
Time (min)
3
6
9

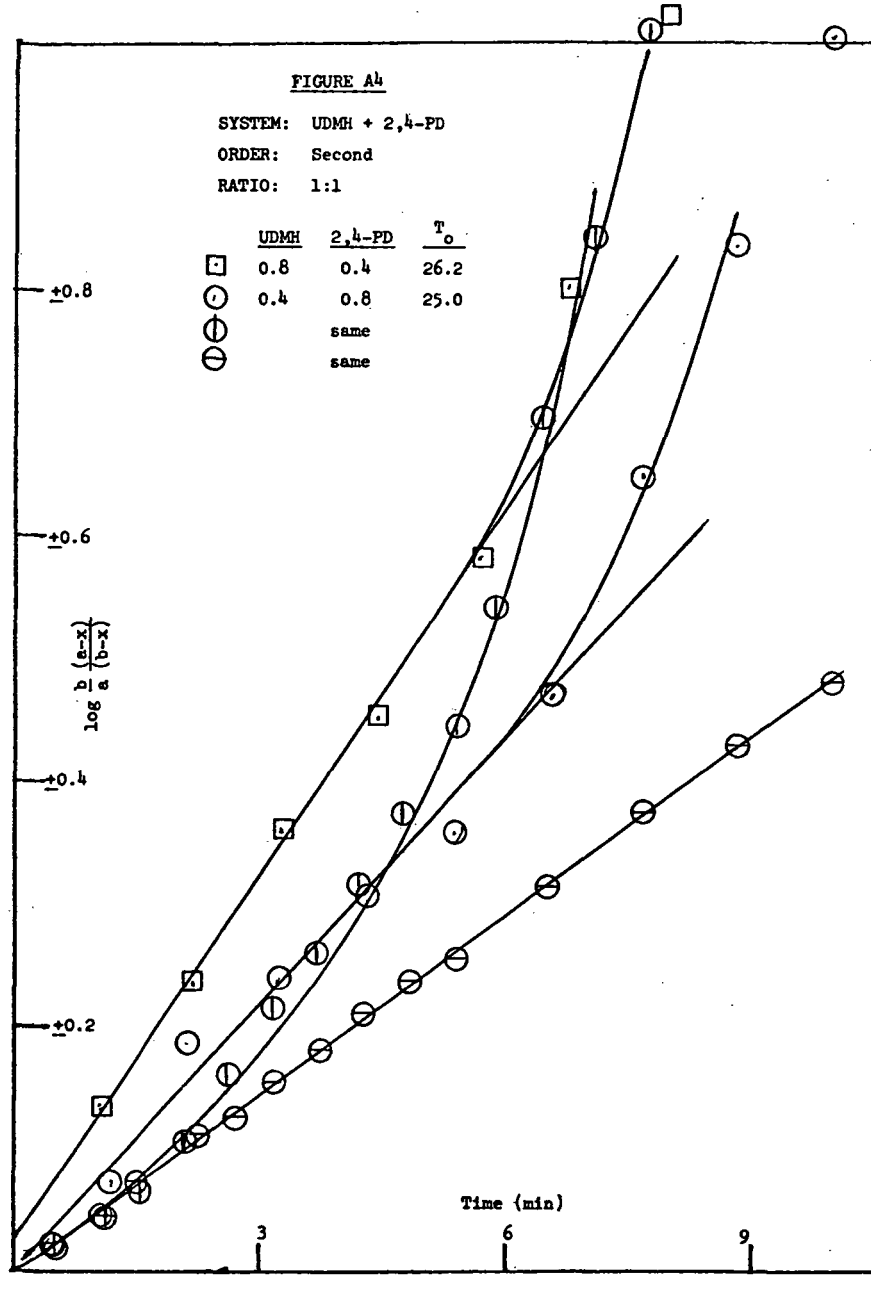
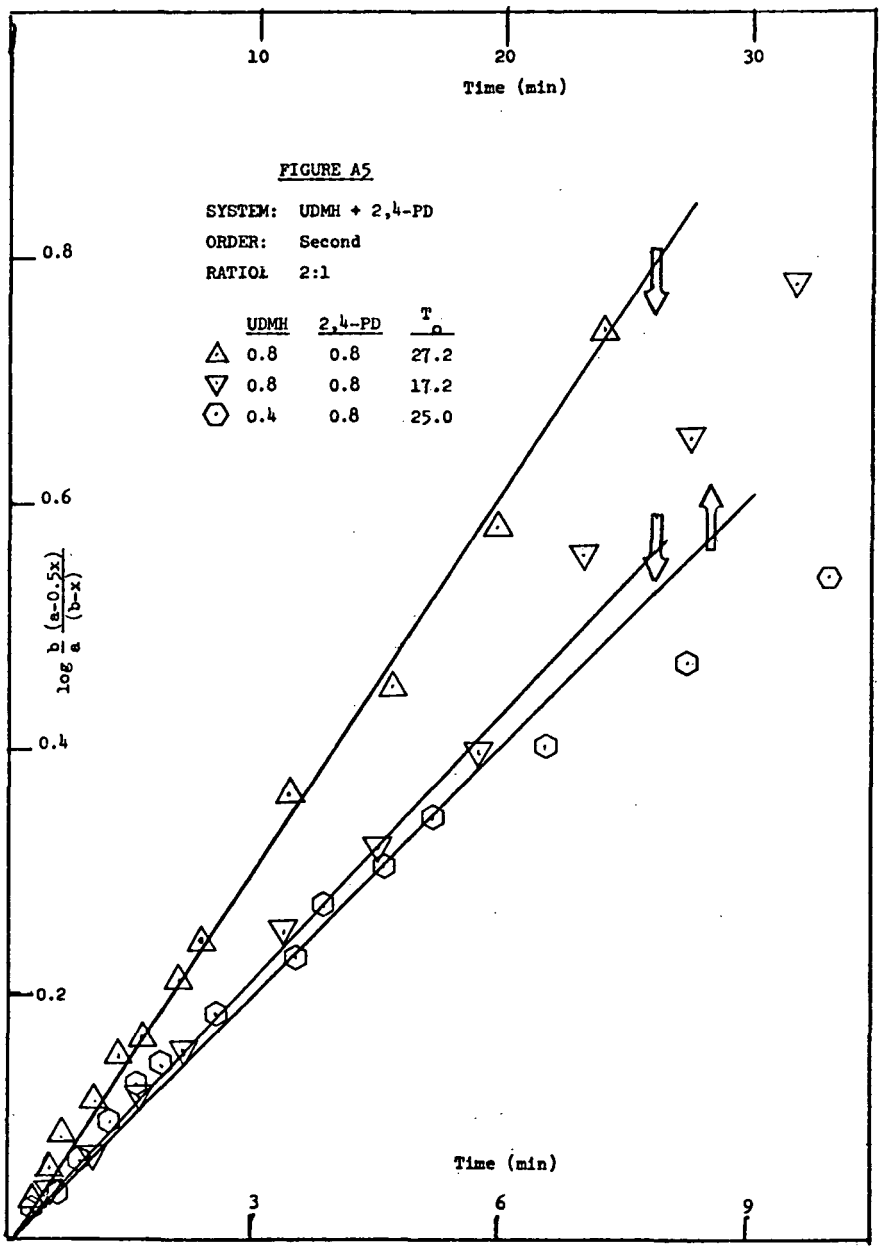


FIGURE A4
SYSTEM: UDMH + 2,4-PD
ORDER: Second
RATIO: 1:1
UDMH 2,4-PD T_o
0.8 0.4 26.2
0.4 0.8 25.0
same
same
±0.8
±0.6
±0.4
±0.2
$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
Time (min)
3
6
9


10
20
30
Time (min)
FIGURE A5
SYSTEM: UDMH + 2,4-PD
ORDER: Second
RATIO: 2:1
UDMH 2,4-PD T_o
0.8 0.8 27.2
0.8 0.8 17.2
0.4 0.8 25.0
0.8
0.6
0.4
0.2
$\log \frac{b}{a} \frac{(a-0.5x)}{(b-x)}$
Time (min)
3
6
9

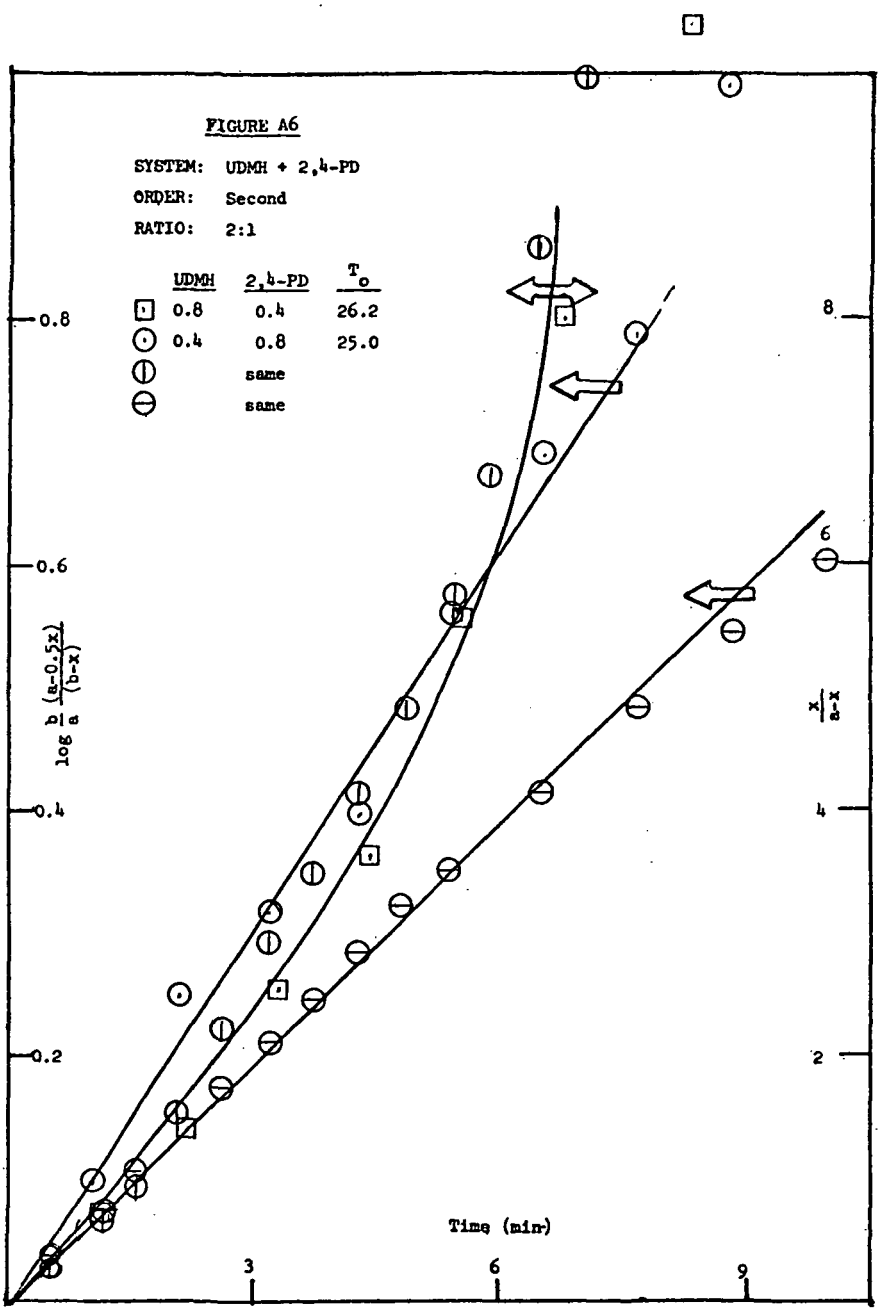
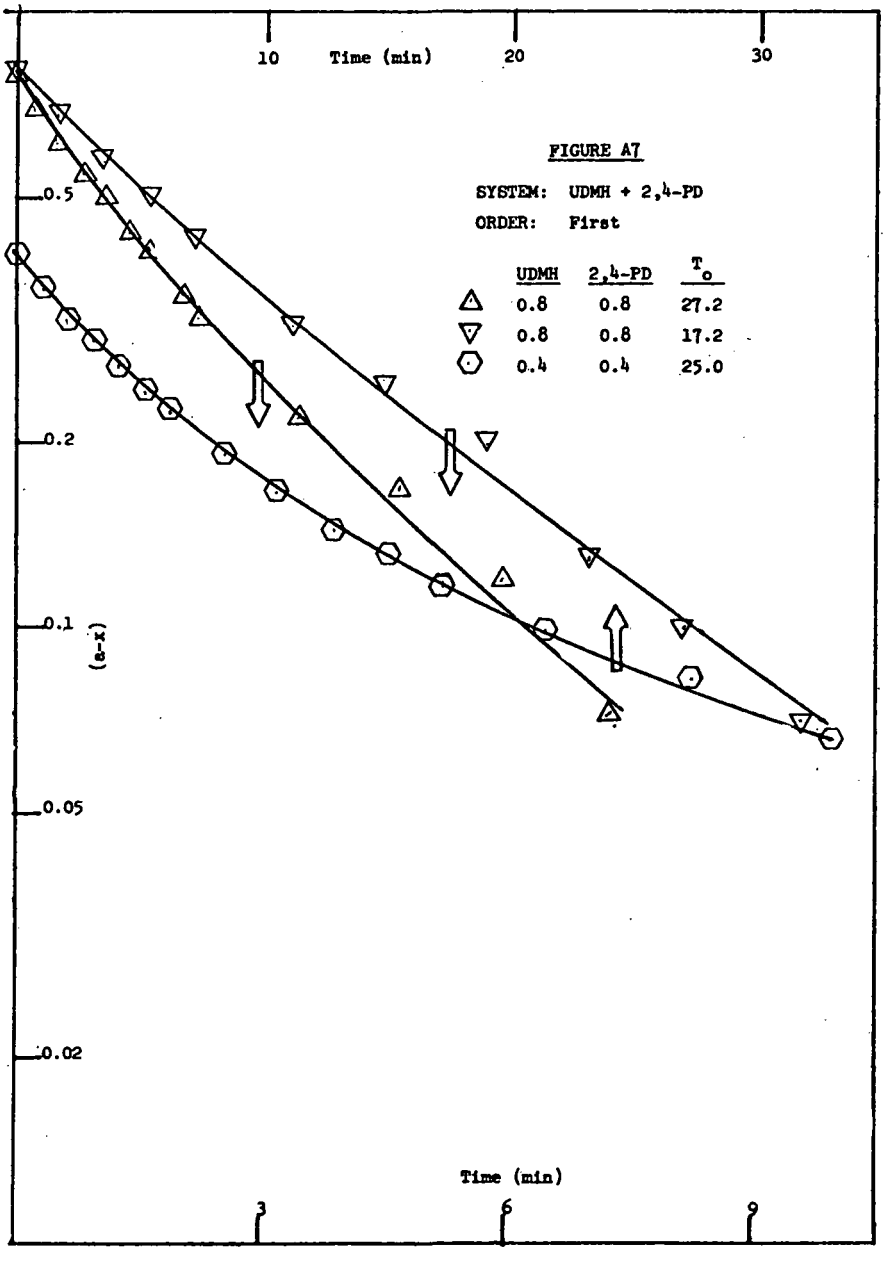


FIGURE A6
SYSTEM: UDMH + 2,4-PD
ORDER: Second
RATIO: 2:1
UDMH 2,4-PD T_o
0.8 0.4 26.2
0.4 0.8 25.0
same
same
0.8
0.6
0.4
0.2
$\log \frac{b}{a} \frac{(a-0.5x)}{(b-x)}$
8
6
4
2
$\frac{x}{a-1}$
Time (min)
3
6
9


10
Time (min)
20
30
FIGURE A7
SYSTEM: UDMH + 2,4-PD
ORDER: First
UDMH 2,4-PD T_o
0.8 0.8 27.2
0.8 0.8 17.2
0.4 0.4 25.0
0.5
0.2
0.1
(a-x)
0.05
0.02
Time (min)
3
6
9

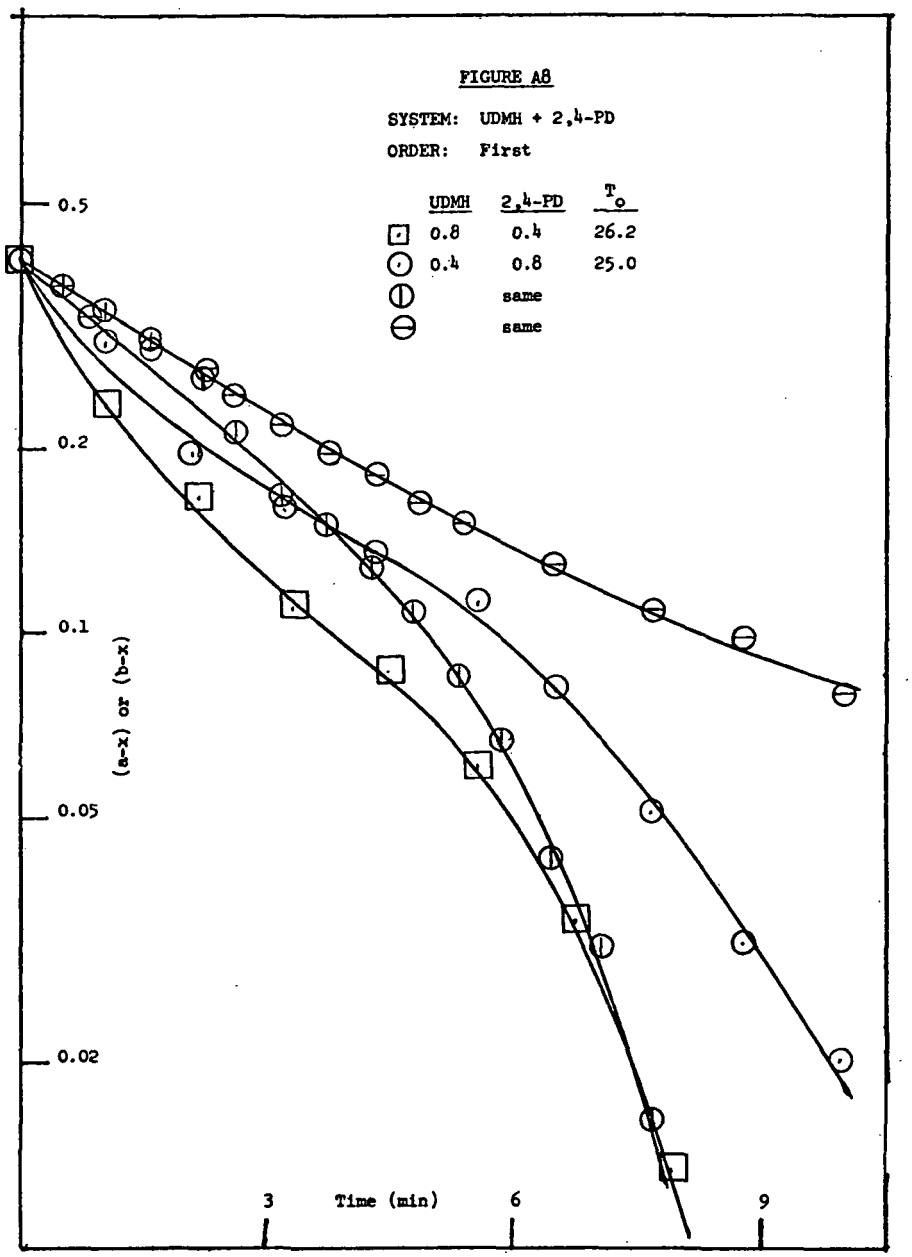


FIGURE A8
SYSTEM: UDMH + 2,4-PD
ORDER: First
UDMH 2,4-PD T_o
0.8 0.4 26.2
0.4 0.8 25.0
same
same
0.5
0.2
0.1
0.05
0.02
(a-x) or (b-x)
3
Time (min)
6
9

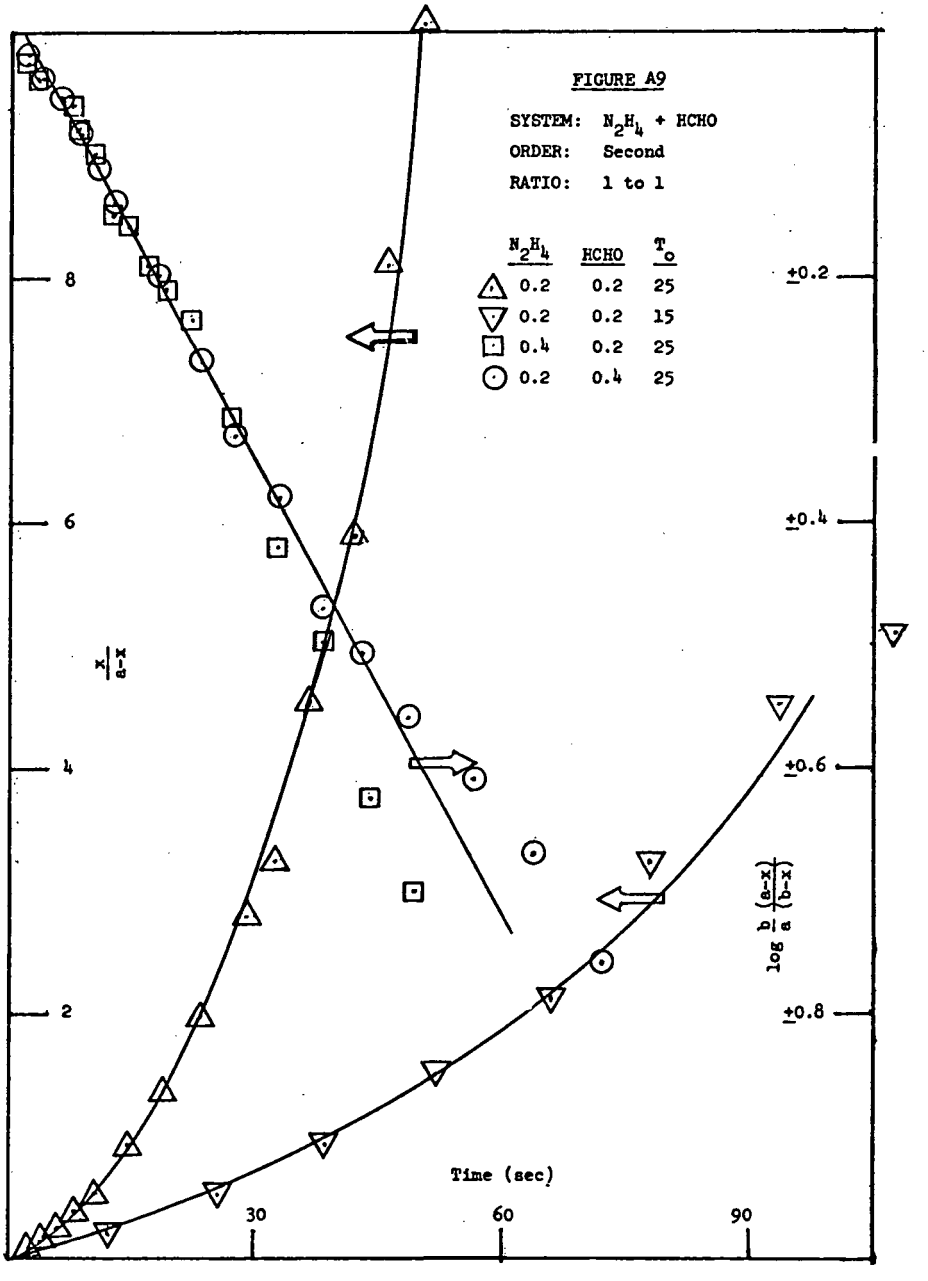


FIGURE A9
SYSTEM: N_2H_4 + HCHO
ORDER: Second
RATIO: 1 to 1
N_2H_4 HCHO T_o
0.2 0.2 25
0.2 0.2 15
0.4 0.2 25
0.2 0.4 25
8
6
4
2
$\frac{x}{a-x}$
±0.2
±0.4
±0.6
±0.8
$\log \frac{b(a-x)}{a(b-x)}$
Time (sec)
30
60
90

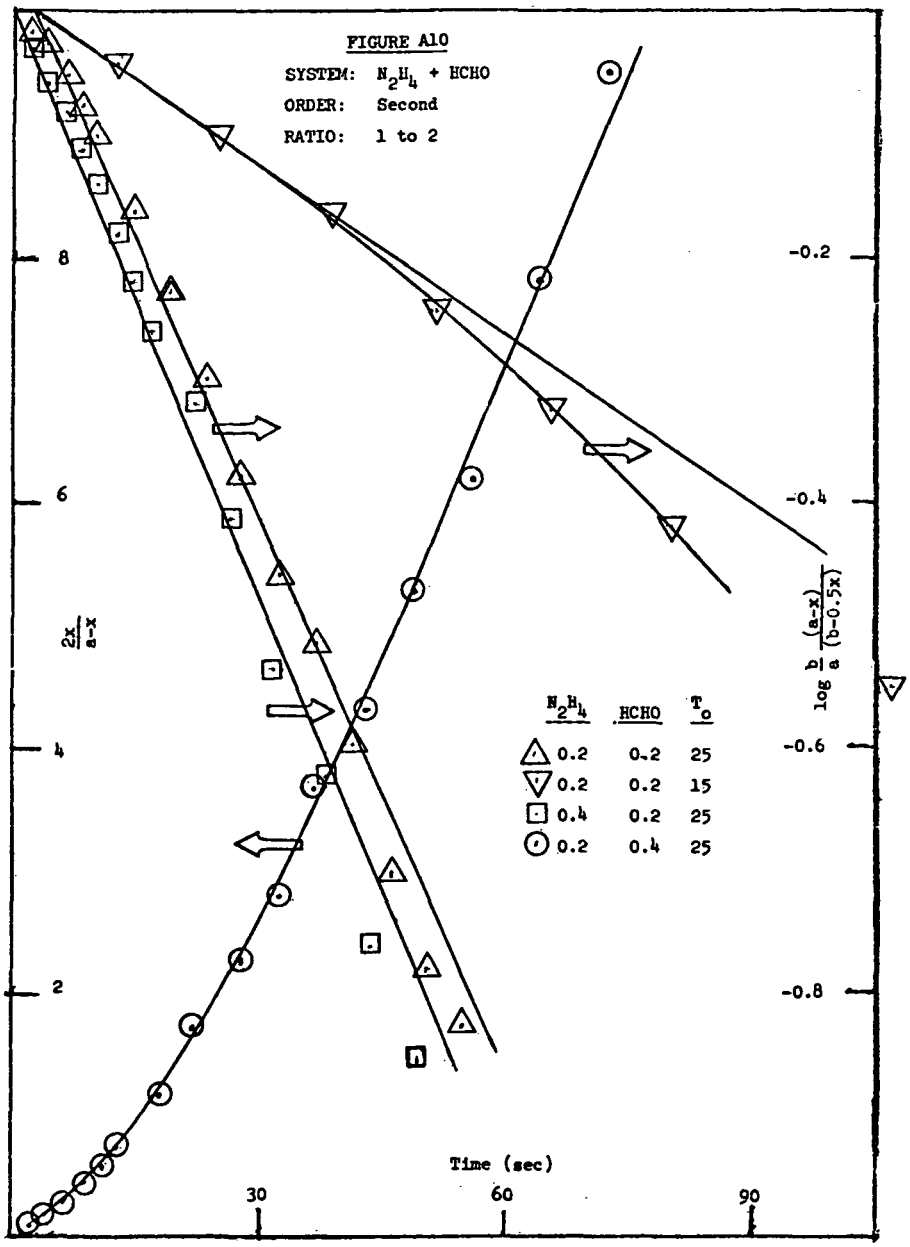


FIGURE A10
SYSTEM: N_2H_4 + HCHO
ORDER: Second
RATIO: 1 to 2
8
6
4
2
$\frac{2x}{a-x}$
-0.2
-0.4
-0.6
-0.8
$\log \frac{b}{a} \frac{(a-x)}{(b-0.5x)}$
N_2H_4 HCHO T_o
0.2 0.2 25
0.2 0.2 15
0.4 0.2 25
0.2 0.4 25
Time (sec)
30
60
90

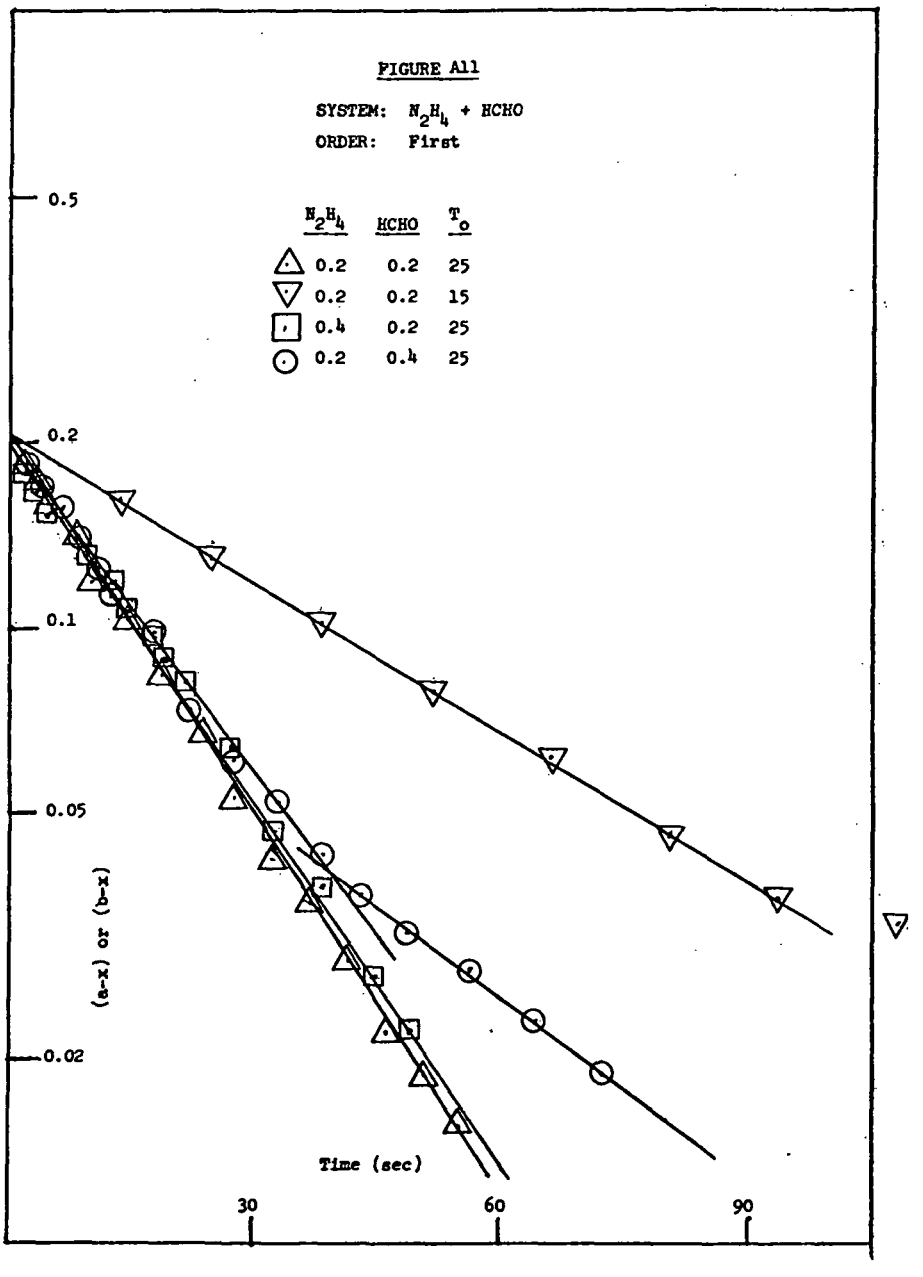


FIGURE A11
SYSTEM: N_2H_4 + HCHO
ORDER: First
N_2H_4 HCHO T_o
0.2 0.2 25
0.2 0.2 15
0.4 0.2 25
0.2 0.4 25
0.5
0.2
0.1
0.05
0.02
(a-x) or (b-x)
Time (sec)
30
60
90

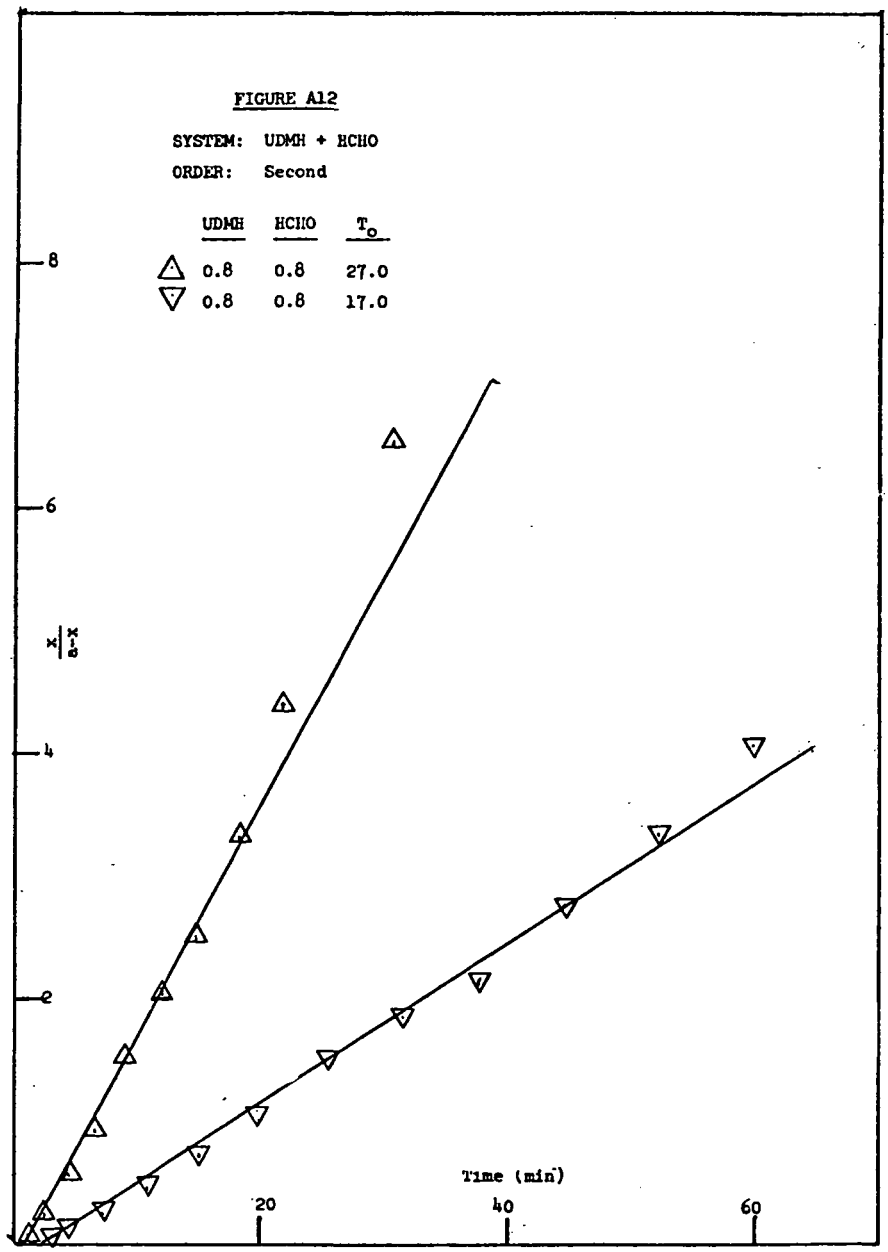
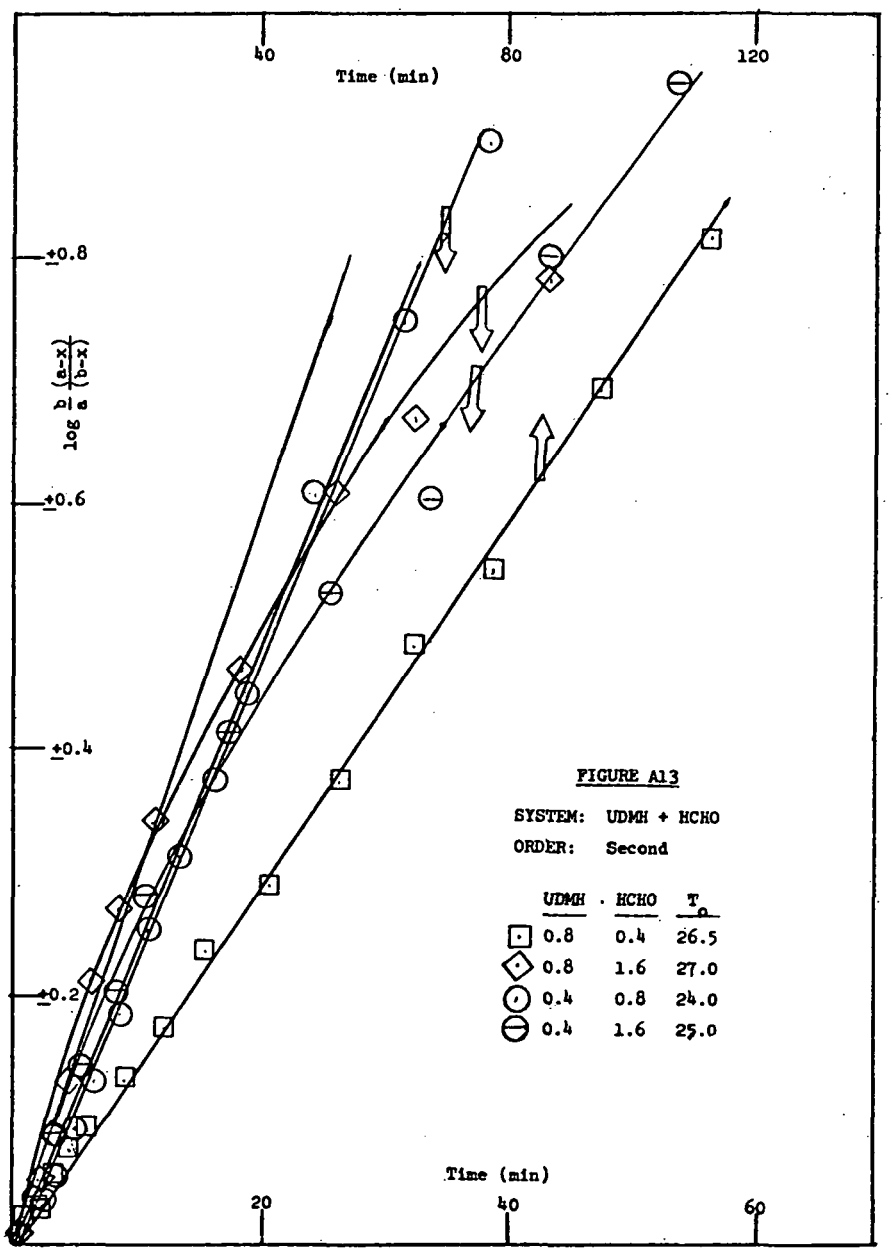


FIGURE A12
SYSTEM: UDMH + HCHO
ORDER: Second
UDMH HCHO T_o
0.8 0.8 27.0
0.8 0.8 17.0
8
6
4
2
x
Time (min)
20
40
60


40
80
120
Time (min)
±0.8
±0.6
±0.4
±0.2
log b/a (a-x)/(b-x)
Time (min)
20
40
60
FIGURE A13
SYSTEM: UDMH + HCHO
ORDER: Second
UDMH HCHO T_o
0.8 0.4 26.5
0.8 1.6 27.0
0.4 0.8 24.0
0.4 1.6 25.0

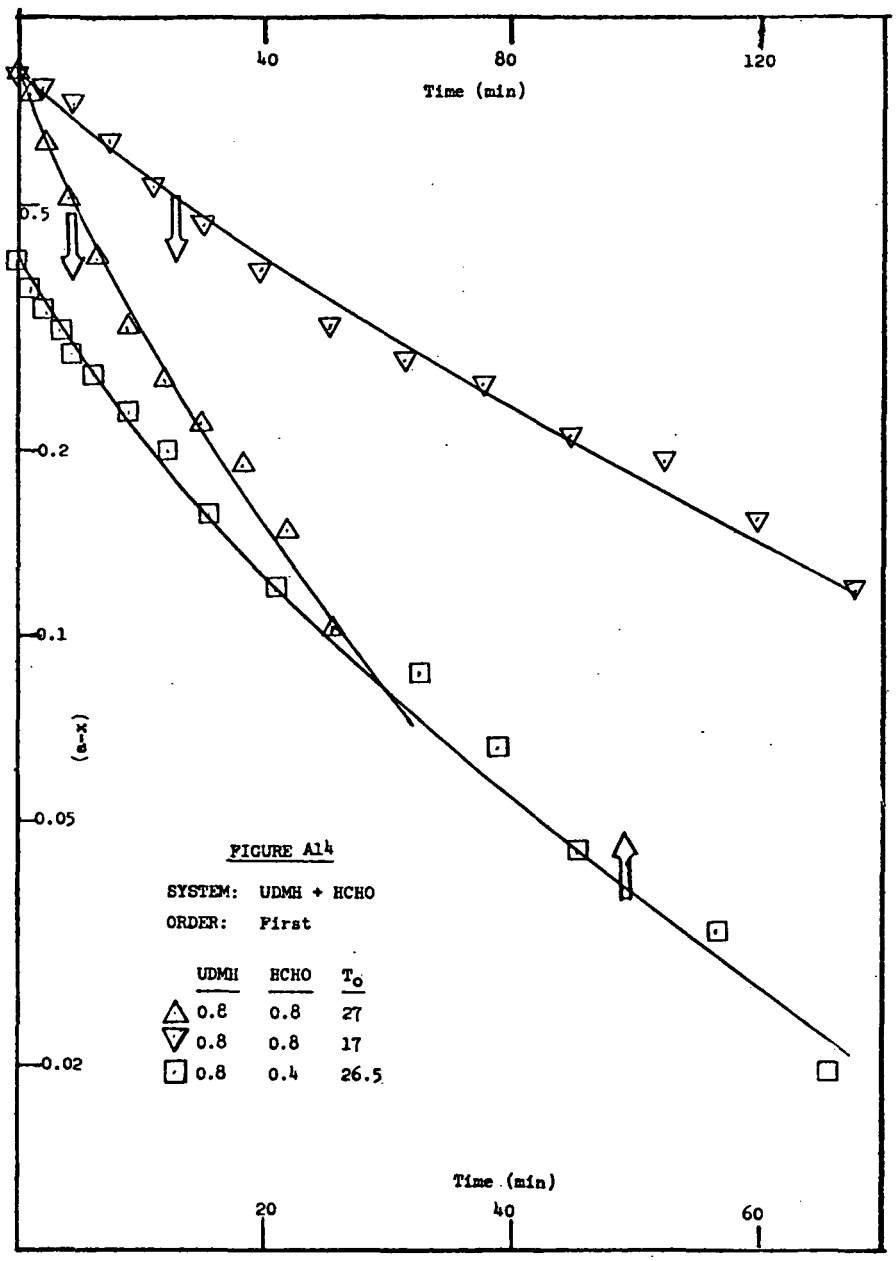


FIGURE A14

SYSTEM: UDMH + HCHO

ORDER: First

	UDMH	HCHO	T_o
△	0.8	0.8	27
▽	0.8	0.8	17
□	0.8	0.4	26.5

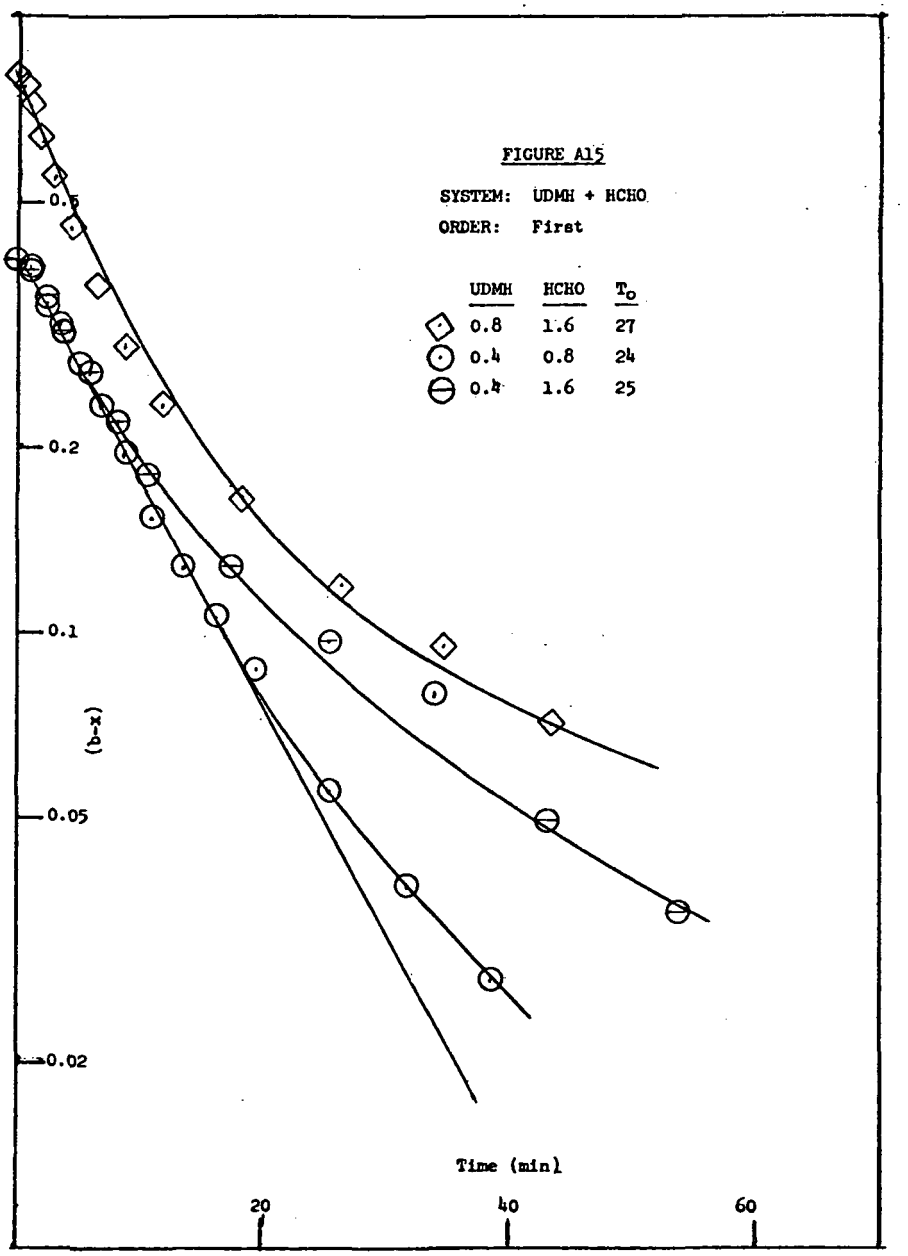


FIGURE A15
SYSTEM: UDMH + HCHO
ORDER: First
UDMH HCHO T_o
0.8 1.6 27
0.4 0.8 24
0.4 1.6 25
0.5
0.2
0.1
0.05
0.02
(b-x)
Time (min)
20
40
60

APPENDIX B

PLANNING REPORT

July 2, 1971

Study to Optimize Gellant Polymer-Water System for Control of Hypergolic Fires

to

National Aeronautics and Space Administration

Ames Research Center

Technical Personnel:

W. C. Foshee
M. F. Katzer
D. C. MacWilliams

Submitted by:

Product Department Laboratory, West
Walnut Creek Research Center
The Dow Chemical Company
Walnut Creek, California

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PLANNING REPORT

Hypergolic Fires

NAS2-6532

INTRODUCTION

Pursuant to the contract #9501 awarded June 11, 1971, a search of pertinent literature has been made to identify the compounds which should be considered in formulating gelled water systems containing scavenging agents for the fuel components. There are numerous degrees of freedom in each of the three major areas of consideration -- chemical, physical and mechanical. The order of precedence in the examination of the variables follows this order, i.e. potential reagents are screened first for chemical properties, then physical properties and finally for compatibility with the mechanical requirements of the system. A material which fails chemical evaluation will not be carried further in the program and likewise a failure on physical grounds will result in rejection for mechanical testing.

A. CHEMICAL IDENTITY OF THE GELLING AGENT

1. Selection of the Agent

There are a number of thickeners available for aqueous systems. Alginates, guar gum, Xanthomonas polysaccharides, methoxylated, hydroxyalkylated and/or carboxylated celluloses and totally synthetic hydrophilic polymers, usually lightly crosslinked. The present study is based on a totally synthetic product, a polyacrylamide crosslinked with methylenebisacrylamide and having approximately 25% of the amide groups hydrolyzed to carboxylate groups. The standard product of this description is sold under the trademark "Gelgard®" by The Dow Chemical Company.

It is the intention of the present study to formulate Gelgard® polyacrylamides with suitable scavengers for fuel components and to demonstrate the effectiveness of such formulations. No effort will be made to study the effects of variations in the polymer structure if the standard polymer will perform satisfactorily. This product has been utilized in the past for thickening water for fire fighting. Other potential thickening agents will be examined only in the event of a total failure of the polyacrylamide gel systems and only with consent of the monitor.

2. Experimental Model for Selection of the Gelling Agent

For a thickener of given chemical identity

Gel Performance α Molecular Weight of Base Polymer (MW)

Density of Crosslinks XL

Degree of Hydrolysis K_{H_2O}

Concentration of Polymer C_G

This series of variables is reduced in number by fixing the polymer identity, molecular weight, crosslink density and degree of hydrolysis. The polymer concentration is the only degree of freedom remaining, hence

Gel Performance = $f(C_G)$.

B. SCAVENGERS FOR N_2O_4

1. By Acid-Base Reaction

The previously established scavenger system for N_2O_4 was sodium hydroxide which is capable of neutralizing both nitric acid (a strong acid) and nitrous acid ($pK_a = 3.4$).

a. The minimum pH of the system: This pH has been fixed at not less than 5.5 to suppress collapse of the gel structure due to

i. protonation of the polymer and

ii. oxidation of the polymer by the nitric and nitrous acids.

b. The maximum pH of the gel system: A base of moderate alkalinity is preferred to a very strong base because:

i. the choice of scavenging reactions for hydrazines is broader

ii. the heat of neutralization of the N_2O_4, estimated to be 22 kcal/g mole using a strong base and neglecting heats of mixing, is reduced by approximately 2 kcal/g mole for each ten fold decrease in the strength of the base and

iii. the weaker base is less corrosive.

c. The equivalent weight of the base: The reaction

$$N_2O_4 + 2\ OH^- \rightarrow NO_2^- + NO_3^- + H_2O$$

is essentially complete at pH>5.5. Inorganic bases which will neutralize N_2O_4 are given in Table I.

d. The solubility of the base: A base soluble in the gel is preferable from an operations point of view since there is no risk of the base separating on standing. However, the high viscosity of the gelled water system permits consideration of the less soluble bases such as magnesium and calcium hydroxides.

e. Side reactions of the base: Ammonia is nucleophilic and will compete with hydrazines for electrophilic scavengers. Hence, ammonia has not been given further consideration.

TABLE I

Bases for Neutralizing N_2O_4

Base	Formula	Grams of Base per Gram N_2O_4	Dissociation Constant (°C)	Solubility g/100 g H_2O (°C)
Lithium Hydroxide	LiOH	0.52	strong base	12.8 (20)
Magnesium Hydroxide	$Mg(OH)_2$	0.63	1.2×10^{-11} (K_{sp}) (18)	0.0009 (18)
Ammonium Hydroxide	NH_4OH	0.75	1.79×10^{-5}	~43 (20)
Calcium Hydroxide	$Ca(OH)_2$	0.81	strong base	0.185 (0)
Sodium Hydroxide	NaOH	0.87	strong base	109 (20)
Sodium Borate	$NaBO_2$	1.43	7.3×10^{-10}	soluble
Sodium Carbonate	Na_2CO_3	2.28 (1 equiv) 1.13 (2 equiv)	5.61×10^{-11} 4.30×10^{-7}	21.5 (20)
Trisodium Phosphate	Na_3PO_4	1.89 (2 equiv)	2.2×10^{-13} 6.2×10^{-8}	11 (20)

f. Gas evolution: Sodium carbonate (and other alkali metal and alkaline earth carbonates) show poor efficiency if neutralized to bicarbonate and evolve a gas (CO_2) if completely neutralized. Gas evolution is not desirable under a layer of gelled water. The scavenger systems are designed to prevent gassing, if possible.

2. By Solid Absorbents

The use of solid absorbents such as limestone, molecular sieves or ion exchange resins has been considered briefly. The necessity of maintaining a relatively high electrolyte level in the gel to prevent gel collapse and low stoichiometric efficiency mitigated against these types of materials. Gel collapse may indeed prove to be a point of failure for alkaline earth oxides which are relatively more soluble than the above named solid absorbents.

3. By Reduction

No suitable reactions for reducing N_2O_4 in alkaline media were located in a brief literature search. Reduction will occur in acid medium but the properties of the gel are adversely affected by strong acids.

4. Evaluation of Alkaline Scavengers for N_2O_4

a. Angle of Repose and Flowability. Gel consistency will be measured by flowing the gel onto a circular panel and allowing the excess to flow over the edge. The thickness of gel at the center of the circle will be measured after

one minute and five minutes and the angle of repose will be calculated.

Gel flow will be measured using a bottle equipped with a pipe such that a half gallon of gel may be flowed at a chosen driving pressure up to 10 psi and the flow time measured. The dimensions of this device will be modified as required to give reasonable flow times.

Some of these experiments will be run at 50°C using gel compositions judged acceptable at room temperature (25°C).

Standard Gelgard® will be dissolved into a solution or slurry of the base to give a system containing 2% Gelgard® polymer. The base will be present in sufficient quantity that (a) 10 g of aqueous gel will neutralize 1 g of N_2O_4 and (b) 40 g of aqueous gel will neutralize 1 g N_2O_4. Additional Gelgard® polymer will be added in small increments to increase the angle of repose of the gel to the required value estimated to be about 6° corresponding to one inch of height per foot of spread. The angle of repose is subject to adjustment based upon the results in the initial fire tests. The effect of a miscible organic compound will be assessed by replacing 10% of the water with acetone.

b. N_2O_4 Neutralization. Formulations containing the lower concentration of base will be evaluated for ability to neutralize N_2O_4 in stoichiometric ratio. A layer of gel 1/2" thick will be placed in a dish with a slightly conical bottom. N_2O_4 will be injected from below by hypodermic syringe. Reaction will be allowed to proceed until all of the N_2O_4 is gone. The angle of repose will be measured and the gel titrated for residual alkalinity to measure the efficiency of N_2O_4 absorption. The experiment will be repeated with the higher level of base using the same ratio of N_2O_4 to gel volume, hence the scavenger will be in four-fold excess.

c. Experimental Model

Angle of Repose (R) depends upon

		Values
Gelgard® Concentration (Volume fraction)	C_G	± 0.02
Identity of the Base	B	LiOH, $Mg(OH)_2$, $Ca(OH)_2$ or NaOH
Quantity of Base (eq/100 ml)	C_B	0.324 or 0.081
Concentration of Organic Solute (Volume fraction)	C_O	0 or 0.1
Temperature of System (°C)	T	25 or 50

Flowability (F) is a dependent variable of R

hence, $R = f(F) = f(B, C_G, C_B, C_O, T)$.

For a given base

$$R = f(C_G, C_B, C_O, T).$$

Expt. No.	C_G (by trial)	C_B (calc'd.)	C_O (vol. fraction)	T °C	N_2O_4 Absorption
1	g_1	0.324	0	25	1:4
2	g_1	0.324	0.1	25	---
3	g_1	0.324	0.1	50	---
4	g_2	0.081	0	25	1:1
5	g_2	0.081	0.1	25	---

This pattern will be repeated for a total of 20 experiments.

C. SCAVENGERS FOR HYDRAZINE AND unsym-DIMETHYLHYDRAZINE

1. Nucleophilic Substitutions and Additions

An extensive literature search has been made to identify reactions of hydrazine and unsym-dimethylhydrazine (UDMH) which are rapid in neutral or alkaline aqueous solution. Data on UDMH are very sparse and many reactions must be inferred from the corresponding reactions with hydrazine. All references refer to Chemical Abstracts, volume and page unless preceded by a journal designation.

Hydrazine and hydroxylamine share in common the structure of a nucleophilic nitrogen atom to which is bonded a second electro-

negative atom. The general effect of the second atom is to increase the nucleophilicity of the first nitrogen in comparison to ammonia and to increase the stability of the adducts of addition reactions. The phenomenon has been referred to the "α-effect" (70, 10770). The effect has been measured for the reactions of hydrazine and UDMH with phenyl acetate.

TABLE II

Dissociation Constants and Rate of Hydrazinolysis of Phenyl Acetate

Large excess of hydrazine, T = 25°C (67, 32095)

	pK_a	$k_n(M^{-1}min^{-1})$
H_2NNH_2	8.26	0.4
$(CH_3)_2NNH_2$	7.56	0.0039

The rate of the reaction with hydrazine is acceptable but the reaction with UDMH is much too slow. On the same scale NH_3 has a rate constant of ∿0.1. The low rate of reaction of UDMH is not fully explained. However, steric effects and decreased electronic density about the $-NH_2$ group are plausible. The lower pK_a value for UDMH as compared to hydrazine is surprising. The usual effect of electron donating alkyl groups is to increase basicity (53, 6989i). The nucleophilic reactions of hydrazine and UDMH are to be examined separately with each substrate.

a. Aldehydes and Ketones. The reaction path with the carbonyl group is usually represented as

$$H_2NNH_2 + O{=}CR_1R_2 \rightleftarrows H_2NNHC(OH)R_1R_2$$

$$\downarrow -H_2O$$

$$H_2NN{:}CR_1R_2$$

Hydrazone

$$H_2NN{:}CR_1R_2 + O{=}CR_1R_2 \rightleftarrows R_1R_2C{=}NNHC(OH)R_1R_2$$

$$\downarrow -H_2O$$

$$R_1R_2C{=}NN{=}CR_1R_2$$

Azine

For UDMH only the hydrazone is possible. These reactions are catalyzed by acid, e.g. acetic. Electron withdrawing substituents at R_1 and R_2 increase the forward rate of reaction. Electron withdrawing groups on the hydrazine (e.g. phenyl hydrazine) retard reaction. UDMH is less basic than hydrazine, hence should react less readily than hydrazine in the first step.

i. Aldehydes-Monofunctional-Aliphatic. Formaldehyde possesses good water solubility and the adduct with hydrazine is fairly stable (70, 10775). Methylal (methyl formal) or paraformaldehyde are alternate forms.

Acetaldehyde is similar to formaldehyde. The azine, $CH_3CH{:}NN{:}CHCH_3$, may be distilled (51, 5054). Acetal and paraldehyde are alternate forms.

Crotonaldehyde is similar and is soluble (18 g/100 g H_2O).

Chloral (Cl_3CCHO) forms a stable hydrate and warrants study if more common aldehydes fail to give stable adducts.

ii. Aldehydes-Monofunctional-Aromatic. Benzaldehyde is soluble only to 0.33 g/100 g H_2O and the Handbook of Chemistry and Physics data table suggests the hydrazone is not stable in water.

o-Nitrobenzaldehyde is very reactive (56, 14125) but the water solubility is low. Other nitrobenzaldehydes are also reactive.

p-Dimethylaminobenzaldehyde has been studied extensively in acid solution (67, 120477). It is insoluble in alkaline medium.

Salicylaldehyde (o-hydroxybenzaldehyde) is soluble to the extent of 1.72 g/100 g H_2O in the acid form. This reagent is reactive but the hydroxyl group suppresses reactivity (56, 14125). No data have been found respective of the reaction in basic medium.

3,4-Dihydroxybenzaldehyde has a water solubility of 5 g/100 g but there are no data on the reaction with hydrazine.

iii. Ketones-Monofunctional-Aliphatic. Acetone reacts more slowly than formaldehyde in acid and has adequate water solubility. The relative rates of these reactions in base are unknown.

Cyclohexanone is more reactive than acetone but water solubility is low (2.4 g/100 g H_2O).

γ-Pyrone ($O(CH=CH)_2C=O$) reacts rapidly (49, 8930d) but is insoluble in water.

iv. Ketones-Monofunctional-Aromatic. Acetophenone is water insoluble but does react. A nitro group accelerates the reaction (52, 11010e).

Benzophenone is very insoluble in water but does react.

Mannich bases, e.g. dimethylaminoethylphenyl ketone will react in alkaline medium but the reagent is water insoluble (52, 2842c) under these conditions.

v. Aldehydes-Difunctional. Glyoxal is known only as a polymer and disproportionates in base. The dioxime may be useful.

Pyruvic aldehyde rearranges in alkali to lactic acid.

Butanone-3-al gives a soluble salt in strong base and appears to be fairly resistant to aldol condensation. The acetal reacts readily with hydrazine in acid (50, 14714b).

γ-Ketovaleraldehyde does not polymerize readily.

vi. Ketones-Difunctional. Diacetyl ($CH_3COCOCH_3$) or 2,3-butanedione aldolizes very readily. It is soluble to the extent of 25 g/100 g H_2O at 25°C and possesses good equivalent weight. Stability of the adducts with hydrazine is unknown.

2,4-Pentanedione (acetylacetone) is soluble to the extent of 12.5 g/100 g of water, is moderately stable in base and reacts with hydrazine to give a hydrazone which can be cyclized to a pyrazole. With UDMA reaction will give the mono- or bis-hydrazones which on heating with alkali yield 1,3,5-trimethylpyrazole (52, 3701h).

2,5-Hexanedione (acetonylacetone) is infinitely soluble in water and will give a bishydrazone with hydrazine which slowly cyclizes to a pyrazine (50, 13937b). UDMH gives the bis(dimethylhydrazone) (52, 3702a).

1,2-Cyclohexanedione gives an unstable derivative with hydrazine (51, 16314b).

1,3-Cyclohexanedione is water soluble and yields stable hydrazones with hydrazine or UDMH (51, 16314b, 52, 3701h).

1,4-Cyclohexanedione is water soluble and yields derivatives with hydrazine and UDMH (52, 3702a). The mono- or bis-hydrazones are possible.

b. Esters and Lactones. The reactions of hydrazines with esters to give hydrazides are generally run under more severe conditions of time and temperature than are the reactions with carbonyl groups. The ease of displacement of the RO group from $ROOCR^1$ increases as R or R^1 becomes more electron deficient (JACS 90, 2622 (1968)). The stability of the hydrazides presumably decreases with increasing electron deficiency in R^1 hence an ester of an aromatic alcohol (phenol) and an aliphatic acid would be a good reagent in principle. In practice, finding such an ester which is also water soluble is difficult.

Hydrolysis of the esters competes with hydrazinolysis if water or OH^- is present.

i. Esters-Monofunctional. Methyl formate is soluble and reacts with hydrazine. Reactions with H_2O and OH^- compete (69, 43172). Methyl formate is soluble (31.9 g/100 g H_2O).

Ethyl acetate is soluble (8.6 g/100 g H_2O).

Phenyl acetate is insoluble (0.032 g/100 g H_2O). Competitive rates of reaction with hydrazine and UDMH are reported (67, 32095).

Methyl benzoate is insoluble (0.016 g/100 g H_2O).

Acetyl salicylate is soluble in the salt form.

ii. Esters-Difunctional. Methyl pyruvate stability in base is in question but it is of potentially high reactivity toward hydrazines. The reaction may produce hydrazide and/or hydrazone.

Methyl acetoacetate is soluble (38 g/100 g H_2O) and will tolerate alkaline media. Products may be the hydrazone and/or hydrazide.

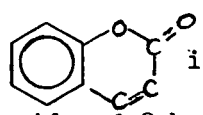
Glycol carbonate (ethylene carbonate) ($\begin{matrix}C\text{-}O\\C\text{-}O\end{matrix}\!\!>\!C{=}O$) reacts. One reference implies the reaction is not rapid (49, 8923) but another suggests the β-hydroxypropionic hydrazide forms readily (53, 9055d).

Methyl oxalate is soluble (6.18 g/100 g H_2O) and has a low equivalent weight on replacement of both ester groups.

iii. Lactones. β-Propiolactone (45, 8031h), or β-methylene-β-propiolactone (48, 1068a) or β-butyrolactone will yield hydrazides. The lactones react with water.

γ-Butyrolactone is infinitely soluble in water and should yield hydrazides from hydrazines.

γ-Valerolactone is water soluble and should yield hydrazides from hydrazines.

Coumarin  is water insoluble. The adduct is the hydrazide of 2-hydroxymethyl benzoic acid (71, 30028).

iv. Thioderivatives. Alkylthioacetate gives a moderate reaction with H_4N_2 (59, 14486) but the products were not given.

δ-Thiovalerolactone gives a fast reaction with H_4N_2 (59, 14486) but the products were not given.

γThiovalerolactone gives fast reaction with H_4N_2 (59, 14486) but the products were not given.

c. Activated Carbon-Carbon Bonds. These scavengers are characterized by having one or more ethylenic or acetylenic bonds conjugated with one or more electron withdrawing groups (Z). The reactions are considered to be Michael-type additions

$$H_2NNH_2 + H_2C{=}CH{-}Z \rightarrow H_2NNHCH_2CH_2{-}Z.$$

With excess electrophilic reagent successive additions occur. The unsymmetrical di-adduct will normally form before the symmetrical derivative but reaction conditions can be modified to control the order of addition (49, 13976). The unsubstituted nitrogen in UDMH is the only one available for reaction. The effectiveness of the activating group based on reactions of RO^- rather than hydrazine decreases in the order

$$PR_3^+ > COR > SO_2R > CN > SO_2NR_2 > CO_2R > CONR_2 > CONH_2 > CONHR$$

(J. Org. Chem. 32, 1091 (1967)).

Many compounds are available within this classification. Only those compounds with significant water solubility will be considered although there are numerous other literature references to reactions of hydrazines with water insoluble, α,β-unsaturated compounds.

Acrolein reacts rapidly with UDMH (55, 8284i). Acrolein acetals should be much less reactive.

Methyl acrylate gives the β-hydrazino derivative with UDMH (66, 85394) but the reaction appears to take 1-2 weeks at room temperature. Hydrazine should react rapidly to give the same product. The water solubility of the ester is low.

Acrylonitrile reacts with hydrazine rapidly (53, 4175a) and UDMH more slowly (51, 17761). The products are β-hydrazinonitriles and polymerize rapidly (59, 13964).

Succinonitrile is very reactive toward RO^-.

Acrylamide is a highly soluble, electrophile, for which no data with hydrazines are known.

Methacrylamide is similar to acrylamide but showed no reaction with RO^- (J. Org. Chem. 32, 1091).

Methylvinyl ketone is over 100 times more reactive than acrylamide (J. Org. Chem. 32, 1091) and the most reactive reagent found for RO^-. Mesityl oxide is unreactive toward RO^-.

Methylvinyl sulfone shows a higher degree of polarization than the sulfoxide in free radical processes. Aryl α-disulfones are more reactive than the sulfoxides (JACS 91, 5516).

Divinyl sulfone reactions with hydrazines have not been reported but reactions with RO^- are rapid (J. Org. Chem. 32, 1091). Both vinyl groups react.

N-Vinylpyridinium fluoroborate is extremely electrophilic consistent with the behavior of neurine (trimethylvinylammonium hydroxide) and trialkylvinylphosphonium derivatives.

2-Vinylpyridine reacts slowly (58, 8013e).

N-Vinylphthalimide and N-vinylsuccinimide react with hydrazine at room temperature to give N-(β-hydrazinoethyl)imides.

d. Organic Halides and Sulfates. The replacement of halogen in polynitrohalobenzenes with hydrazine to yield hydrazobenzenes will proceed at room temperature over a period of days (51, 12888b, 53, 6119a). However the reagents are not water soluble. Sulfonamide groups may replace the nitro groups (70, 57342).

Benzyl chloride requires refluxing to yield benzylhydrazine (52, 9071c). The kinetics of the reaction with benzyl iodide

and alkyl halides show no "α-effect" and the rates are correlatable with the basicity of the amines (71, 21384).

Chloroacetic acid will react with hydrazine over a two-day period (54, 15230f) to give α-hydrazinoacetic acid.

ß-Chloropropionitrile may react rapidly (70, 19410). The original paper is ordered.

The reaction with methyl iodide in water at 25°C has a second order rate constant of 1.1×10^{-3} M^{-1} sec^{-1} and E_A of 20.2 kcal (70, 86759). This reaction is about one order of ten slower at 25°C than is needed for a practical scavenger.

Dimethyl sulfate reacts with hydrazine to give the series of methylhydrazines up through three methyl groups. The reaction appears to be fairly rapid (60, 1588b).

e. Alkylene oxides. The reaction of hydrazine with ethylene oxide to give ß-hydroxyethylhydrazine occurs in several hours at room temperature.

Propylene oxide reacts at 70°C (49, 6099).

Epichlorohydrin is not mentioned in the hydrazine literature.

Halohydrins react with hydrazines at unknown rates (49, 6099).

Ethyl glycidate requires heating to react rapidly with hydrazine (58, 4542g).

The reaction of hydrazine with 1,2-epoxy-3-methyl pentyne-3 is vigorous (55, 19896c).

The reaction of hydrazine with butadiene dioxide yields trans-4,5-piperidazine at room temperature (57, 6825a).

Cyanohydrins are simply excluded by toxicity.

f. Acid Halides, Acid Anhydrides and Imides. In general, these compounds are believed to be too reactive for use in aqueous alkali.

Benzoyl chloride is not sufficiently soluble in water. However, this reagent is used to benzoylate amines in aqueous alkali (Schotten-Baumann reaction).

Succinic anhydride gives the mono- and di-hydrazides of hydrazine from ethanol (47, 494c). The reaction with hydrazines in water is not known.

g. Other Compounds. Compounds containing the C=S grouping as thioacid or thioketone will react, usually with the loss of H_2S. One example of reaction with an amidine was found.

2. Acid-Base Systems

The acidity constants of nitrous acid (pK_a=3.4) and of hydrazine (pK_a=8.26) and UDMH (pK_a=7.56) are sufficiently separated that a buffer system operating at or near a pH of 5.5 may trap substantially all of the fuel and oxidant components as the corresponding salts. Monosodium succinate (MW=140) is quite soluble and provides a buffer in the pH range of 3.2 to 6.6. Similarly, the acetic acid-sodium acetate system is effective over the pH range of 3.75 to 5.75. This concept was not considered in the original proposal and will not be developed in this study unless the scavenger techniques as originally proposed prove to be impractical.

3. Oxidation in Alkaline Solution

In the course of the literature search for scavenger agents references to the oxidation of hydrazine in aqueous alkaline solution were found. Oxidants included dissolved oxygen (65, 6358c), hydrogen peroxide catalyzed with metals such as cupric copper (46, 9959f, 70, 23581) or iodide (47, 10324i), cumene hydroperoxide catalyzed with iron (III) EDTA complex (55, 27182e), ferricyanide (48, 13521, 52, 12650), mercury (II) EDTA complex (55, 14174b), potassium permanganate (50, 10608f, 51, 2470a), and iodine monochloride (54, 17156e).

These reactions will not be investigated further in this study unless the scavenger techniques as originally proposed prove to be impractical.

4. Evaluation of Electrophilic Scavengers for Hydrazine and unsym-Dimethylhydrazine

a. Kinetic Model. All of the reactions chosen for hydrazine and UDMH deactivation are nucleophilic displacements or additions. These reactions are usually overall second order, first order in the hydrazine and first order in the electrophile, hence

$$\frac{dx}{dt} = k(a-cx)(b-x)\exp\ \frac{-E}{RT} \qquad (1)$$

where x is the amount reacted at time t, k is the rate constant, a is the concentration of hydrazine and b is the concentration of electrophile at time zero, c is the stoichiometric proportionality factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

For $a \leq b$ and c=1

$$\text{At } x=0 \quad T=T_1 \qquad (2)$$

$$x=a \quad T=T_2 \qquad (3)$$

Assuming the temperature rise of the reaction is proportional to conversion, then the temperature at any conversion, T_x is given by

$$T_x = T_1 + \frac{x}{a}(T_2-T_1) \qquad (4)$$

The instantaneous value of the exponential term in equation (1) is given by $-E/RT_x$. The ratio of the rate constant at x=0 to the rate constant at any conversion is therefore given by

$$\frac{k}{k_o} = \exp \frac{-\frac{x}{a}(T_2-T_1)}{T_1^2 + \frac{x}{a}(T_2-T_1)T_1} \cdot \frac{E}{R} \qquad (5)$$

If T_2-T_1 is small compared to T_1

$$\frac{k}{k_o} = \exp \frac{-\frac{x}{a}(T_2-T_1)}{T_1^2} \cdot \frac{E}{R} \qquad (6)$$

If a is in excess, equations 3-6 are formulated using b instead of a. If the stoichiometry is other than 1:1 the appropriate stoichiometric proportionality factor is inserted in equations 1, 4, 5 and 6.

For orders other than second order, trial and error fitting of the data for several experiments will usually yield the apparent order of reaction. If two reactions are occurring simultaneously at different rates or consecutively an additional set of terms identical in form to equation 1 must be included. A mathematical analysis of such a reaction system is very difficult but not impossible. Equation 1 combined with equation 6 gives a power series upon integration hence the integration of the differential form by finite increments is the most convenient method for handling the data.

The expected heats of reaction of the hydrazines with the electrophiles are 5-15 kcal/g mole. The heat capacity of the calorimetric system (which will be calibrated) will be largely due to the water which has a nominal heat capacity of 1 cal/g. Allowing for a 20% reduction in this value for the glass of the container and the lower heat capacities of the organic components the expected temperature rise for each kilocalorie released in the reaction of components at 1 M concentration is ~0.8°C. Thus a 3°C rise in temperature represents a ΔH of -3.6 kcal/g mole. The maximum possible free energy change would be -3.6 kcal/g mole which corresponds to an equilibrium displaced 95% toward products. In fact, the process is spontaneous so the free energy change would be less and the reaction less complete. Thus a criterion of a minimum of a 3°C rise in temperature exclusive of the heats of mixing which appear almost instantaneously is a minimum restriction on the completeness of reaction.

b. Evaluation of Scavengers for Hydrazines. The aqueous-base combination established for N_2O_4 scavenging will be employed for screening electrophilic reagents. If this system is a strong base, one additional experiment will be run with a weak base to insure that the strong base is not stopping the desired reaction. The gelling agent will be omitted. The volatility of the anticipated product(s) of reaction will be estimated. A calorimeter consisting of a thermos bottle

with appropriate ports for additions of reagents, a stirrer and a thermocouple attached to a recorder will be assembled. Hydrazine and UDMH will be reacted at initial concentrations of 1 M in the calorimeter with a 1 M solution of the electrophile in the aqueous-base medium. If there is no significant temperature rise (<3°C) in 15 minutes the experiment will be terminated. Those reagents showing the most rapid and largest temperature rises will be evaluated after standing in contact with aqueous-base for 4 hours. Those electrophiles which remain active after this treatment will be studied at three ratios of reactants and at one additional starting temperature. These experiments will provide enough data to estimate the rate constant, the activation energy, the stoichiometric ratio and the order of reaction using equation 1. The kinetic result will be checked in the presence of the gelling agent to insure that the gelling agent is not interfering with the reaction when the reactants are intimately mixed.

The absorption of Aerozine 50 in a layer of gel containing a hydrazine scavenger will be run in the same manner as the absorption of N_2O_4 by gel. The scavenger content of the gel will be adjusted to react with 80% and 100% of the Aerozine 50. The absorption rate will be monitored qualitatively and the gel examined for collapse. Material which is absorbed will be assumed to have reacted following the predictions of the reaction rate studies. Dye will be used in the Aerozine 50 to aid observations if necessary.

A brief review of the literature suggests the most convenient method for analysis of hydrazine-UDMH-reaction products-water mixtures is by gas chromatography. Oxidation procedures lack specificity and the spectrophotometric methods require drastic reductions of pH which will probably affect reaction rates and equilibria.

The recommended column for separating hydrazine and UDMH is 25% Carbowax 400 on Chromasorb P pretreated with 7% KOH (68, 35641, 68, 84136). An earlier reference recommended Celite C22 as the support (65, 12886c). Water behavior on these columns is unknown. Dowfax 9N9 on a Teflon 6 support will separate water from hydrazine but not UDMH (65, 7982). Satisfactory separation of water, hydrazine and UDMH is claimed for a column of 10% 2-hydrazinopyridine on Fluoropak 80 support but this column was usable only 6-10 days (67, 78636).

The Carbowax 400 on alkaline Chromasorb P will be tried. If the column does not work this phase of the project will be terminated. It is hoped that thermal instability of the derivatives may be detected by the appearance of abnormal amounts of starting materials or by smeared out elution peaks. Derivatives with undesirably high volatility may also be detected. Analytical evaluation will be applied only to systems which are under consideration for detailed kinetic study.

c. Experimental Model.

Rate of Reaction $\frac{dx}{dt}$	α	Nucleophile	N
		Electrophile	El
		Concentration of Nucleophile	C_N
		Concentration of Electrophile	C_{El}
		Initial Temperature	T_o
		Alkalinity	pH
		Lapse Time	t_l
		Viscosity	η

i. Initial Screening of Electrophiles Against Hydrazine.

(N, C_N, C_{El}, T_o, t_l and η are constant).

$\frac{dx}{dt} = f(El,pH) \geq 0.3$ M min.$^{-1}$ and $\Delta T \geq 3°C$.

Expt. No.	Electrophile	pH
1	El	strong base
2	El	weak base

The electrophiles listed in Table III will be screened for reactivity.

TABLE III

LIST OF ELECTROPHILES SELECTED FOR EVALUATION

Group	Electrophile	Equivalence (g. of El/g. Aerozine-50) Monofunctional	Difunctional
a.	Formaldehyde	0.65	
	Acetaldehyde	1.0	
	Salicylaldehyde	2.7	
	Cyclohexanone	2.1	
	Butanone-3-al	1.9	
	2,4-Pentanedione	-	1.1
	1,3-Cyclohexanedione	-	1.2
	1,4-Cyclohexanedione	-	1.2
	Methyl formate	1.3	
b.	Acetyl salicylate	3.9	
	Methyl pyruvate	2.2	
	Methyl acetoacetate	2.5	
	Propiolactone	1.6	
	γ -Butyrolactone	1.9	
	γ -Thiovalerolactone	2.3	
c.	Acrolein	1.2	
	Succinonitrile	1.7	
	Methylvinylketone	1.5	
	Divinylsulfone	-	1.3
	N-vinylpyridinium borate	3.6	
	or trimethylvinylammonium hydroxide	2.2	
	or trimethylvinylphosphonium chloride	3.0	
d.	β -Chloroacrylonitrile	1.9	
e.	1,2:3,4-Butadienedioxide(*)	1.0	
f.	Succinic anhydride	2.2	

(*) corrected in proof

ii. Initial Screening of Electrophiles Against UDMH.

(N, C_N, C_{El}, T_o, t_1 and η are constant).

$$\frac{dx}{dt} = f(El,pH) \geq 0.3 \text{ M min.}^{-1} \text{ and } \Delta T \geq 3^{\circ}C.$$

Only the electrophiles passing screening with hydrazine will be evaluated.

iii. Effect of Solution Time on the Electrophile.

(C_N, C_{El}, T_o and η are constant). The electrophile will be held in the aqueous alkaline medium in a closed vessel for 4 hours and evaluated against the hydrazine of lowest activity.

$$\frac{dx}{dt} = f(N, El, pH, t_1) \geq 0.3 \text{ M min.}^{-1}$$

The two most reactive electrophiles having acceptable stability will be evaluated further.

iv. Kinetic Evaluation. (N, El, and t_1 are constant.)

$$\frac{dx}{dt} = f(C_N, C_{El}, T_o, \eta)$$

The ratio of C_N/C_{El} will be adjusted to match the expected stoichiometry. The actual stoichiometry, rate constant and activation energy will be estimated for each hydrazine.

Expt. No.	N	El	C_N (M)	C_E (M)	T °C	η cps.
1	N_1	El_1	0.5	1.0	25	~0.9
2	N_1	El_1	1.0	1.0	25	0.9
3	N_1	El_1	1.0	0.5	25	0.9
4	N_1	El_1	1.0	1.0	35	0.8
5	N_1	El_1	1.0	1.0	25	1000^+
6-10	N_2	El_1		5 experiments		
11-15	N_1	El_2		5 experiments		
16-20	N_2	El_2		5 experiments		

Doubtful experiments will be duplicated.

v. Evaluation of Interfacial Diffusion.

(N, C_N, T_o and t_1 are constant.) This experiment is qualitative. The amount of Aerozine 50 is fixed at 2.5 ml (estimated 0.049 mole) per 100 ml of gel.

$$\frac{dx}{dt} = f(C_{El}, pH, \eta).$$

Expt. No.	Electrophile Compound	Concentration equiv/100 g gel	pH[(a)] Condition
1	El_1	0.040	hi
2	El_1	0.049	hi
3	El_2	0.040	hi
4	El_2	0.049	hi
5	El_1	0.049	lo
6	El_2	0.049	lo

Note (a): If the lower pH condition is found to be essential Experiments 1-4 only will be run at the low pH.

D. FIELD OPERATIONS

The field operations are predicated upon laboratory results insofar as selection of reagents is concerned.

1. The efficiency of the gel system will be evaluated as a function of the following variables.

    a. Gel consistency
    b. Rate of gel delivery
    c. Design of gel delivery system and a nozzle
    d. Configuration of the fire
    e. Rate of mixing of fuel components
    f. Gel/fuel ratio
    g. Gel/oxidizer ratio
    h. Pattern of gel delivery
    i. Ability of gel to prevent reignition
    j. Ability of gel to suppress fuel-air fire

2. Experimental Model. No model has been developed for this phase of the study. The initial investigations will proceed in the order indicated above.

E. SAFETY

A safety manual for field operations has been written and is being evaluated. Mixtures of fuel components with gel systems which are recommended for field use will be tested by DTA for stability when evaporated to dryness and heated. These mixtures will not be used in field work if evidence of explosive decomposition is found.

III. FIELD STUDIES

By

W. C. Foshee

SUMMARY

An aqueous system has been developed to deactivate one gallon quantities of nitrogen tetroxide and Aerozine-50. Over 75 field tests have been conducted on spills involving as much as one quart of each propellant.

Spill procedures were developed to simulate two conditions. Tubing breaks and fuel tank punctures on board the command module were simulated by controlled propellant flow into the test pan. Sudden spills from a ruptured tank were simulated by sequential dumping of propellant into the test pan.

Two sets of tactics were developed for control of the two spill conditions. A very viscous formulation of a gelled water system and an ungelled aqueous fog is used in the situation of simultaneous propellant flow. The gel is used as a dam to separate the hypergolic components and to help control the oxidizer fumes. Because the fuel will continue to burn in air, it requires additional control. A fog of ungelled aqueous suppressant can be effectively used on the fuel without disrupting the gelled suppressant. A buffer of one molar acetic acid and one molar sodium acetate is recommended for the aqueous phase of both systems. A concentration of 3.7% GELGARD® M polymer should be used to gel the buffer for separation of propellants and for N_2O_4 control. The temperature of the gel system must be below 60°F in order to be effective.

A slightly different technique is used for the sudden spill. If possible, an effort is made to contain the spilled propellant by surrounding it with the gelled water system. The propellant is then covered with additional gel. A less viscous gel, 3% GELGARD® M polymer in the buffer, is desirable for this system. The lower viscosity gel is adequate for containing the spill and it can mix more readily with the A-50 than a very viscous gel. This neutralizes the propellant and eliminates the possibility of fire and explosion caused by subsequent propellant spillage.

Under the first condition, that of continuously flowing propellants, additional studies should be conducted. More dependable control of the air oxidized A-50 fire is desirable. An evaluation of suppressants normally used for air oxidized fires involving common fuels (e.g., gasoline) should be included in future work. The suppressant should be designed for delivery to the fuel without disrupting the gel used to separate the two propellants and to control the N_2O_4. Both fogs and foamed suppressants would appear to meet these criteria. A foam should have the additional advantage of superior blanketing properties for A-50 in air fire control. For maximum control and safety, the gelled system should be handled by one person and the A-50 control system should be handled by another person.

INTRODUCTION

Small quantities of toxic hypergolic rocket propellants, specifically N_2O_4 and Aerozine-50, may be spilled from the command module as a result of a "hard" landing. In order to abort a mission during the final launch stage, a Launch Escape System is activated. As a part of the Launch Escape System, most of the propellant is blown out with helium before the command module hits the ground. However, a propellant system failure caused by a hard landing would release the remaining propellant (about one gallon). This would result in a toxicity and fire hazard to the astronauts.

Accidental propellant releases also occur on the launch pad. Malfunctions during loading operations may result in spills of about one gallon of propellant. Most of this hazard is produced by propellant draining from fueling lines.

In order to reduce the hazards caused by propellant spillage, it is not only necessary to control fires, but also to control the corrosive and toxic fumes. The current fire fighting procedure is to push the propellants away from critical areas with a spray of water. Since the water runs away, separation of flowing propellants requires constant application. This would make it difficult to control secondary or scattered areas of burning propellant. Although fire control is a major consideration, the toxicity and fuming problems are also serious. Water, itself, does little to alleviate these secondary problems.

Preliminary experiments indicated that gelled water systems might improve control by separation, entrapment, and neutralization. Our laboratory program eliminated extensive field screening by identifying the most likely materials to use for propellant neutralization. The importance of temperature control was another item that was noted during the laboratory studies.

After assembling mixing equipment and establishing that small spills might reasonably represent larger spills, considerable effort was expended to develop gel delivery systems. The main objective of the field operations was then to define the best set of tactics to use with the system designed for optimum control of the spill.

SYMBOLS AND ABBREVIATIONS

NASA - National Aeronautics and Space Administration
KSC - Kennedy Space Center
LES - Launch Escape System
N_2O_4 - nitrogen tetroxide
UDMH - unsymmetrical dimethylhydrazine
A-50 - Aerozine-50 (50:50 mixture of UDMH and hydrazine)
B.P. - boiling point
Temp. - temperature
Fig. - figure
Reh. - rehearsal
No. - number
max. - maximum
psi - pounds per square inch
ΔP - pressure drop
gpm - gallons per minute
ppm - parts per million
gal. - gallons
cc - cubic centimeters
sec. - seconds
min. - minutes
hr. - hours
in. - inches
ft. - feet
" - inches
' - feet
I.D. - inside diameter

EXPERIMENTAL PROGRAM

a. GENERAL FIELD SET-UP AND MIXING PROCEDURES

1. General Field Set-Up

A test site was constructed at The Dow Chemical Company's manufacturing plant in Pittsburg, California. A plan view of the test area is shown in Figure 1. In addition to the 100 gallon Pfaudler, two small pressurized tanks (a 6 gallon and a 12 gallon tank) were located by the fire pan. The original plan was to mix about 50 gallons of gel at one time and run 3 to 4 tests from each batch. Since changes in the gel formulation became one of the more critical factors, smaller tanks were used to simplify evaluation of these variations. Nitrogen gas pressure (about 100 psi) was used to deliver the gel to the fire.

The fire pan was designed after consultation with NASA Fire Protection at KSC. The group at KSC had tried both stainless steel and mild steel. Heat distortion had rendered their stainless steel pan unuseable. Mild steel was chosen for our fire pan. The dimensions are 3 x 6 x 0.5 feet. The pan was sloped 0.5 degrees to a two-inch drain. Although iron oxide can initiate spontaneous decomposition of A-50, (1) this did not occur in our testing program. In order to prevent premature vaporization of N_2O_4 (B.P. = 21.1°C[2]) the fire pan was surrounded by an ice bath.

The N_2O_4 was supplied and stored in 10 pound and 120 pound cylinders. Graduated cylinders were used to measure the amount used for each test.

Five gallons of each fuel component was stored under a 3-5 psi nitrogen blanket in 304 stainless steel tanks. The hydrazine and UDMH were stored separately and mixed as needed for testing. Nitrogen pressure was used for transferring the fuel to graduated cylinders.

Two 16 mm movie cameras were available to record the test program. Most of the record was made with one camera using color movie film at 24 frames/second.

2. Mixing Procedures

The general procedure used for mixing the gelled supressant was to add the sodium acetate to an amount of water equal to about 1/2 the total volume desired. After the sodium acetate dissolved, the acetic acid was added and the solution was brought to final volume

by adding water and ice as required to maintain the temperature between -5°C and 0°C. If an A-50 scavenger was desired, it was added before the last quantity of water and ice.

Dry polymer was added to the chilled buffer solution as it was pumped through a powder disperser (Figure 19). The polymer was allowed to hydrate at least two hours before using for fire control. At low temperatures (below 15°C) the hydration time is especially important. It is necessary to agitate the solution until it has enough viscosity to maintain uniformity.

The gel quality (flow index and slump) was measured according to the procedures described in the laboratory section of this report under "Scavengers for Nitrogen Tetroxide - Experimental".

b. SCALING STUDY AND UNCONTROLLED FIRES

Development of a realistic fire situation was of utmost importance to this study. Simultaneously dumping the fuel and oxidizer together represents the extreme of energy release for the propellant system. As can be seen from Test No. 1 in Table 1, suppressing the explosion while it is occurring is not feasible. A lower intensity or even prevention may have been possible if suppressant were applied in advance. If the flow of fuel and oxidizer is too slow or the mixing is insufficient, the energy output will be insignificant.

Since the KSC rescue team works with a 3 to 6 minute rescue goal, it would be convenient to use a time shorter than 3 minutes. The time should be at least 0.5 to 1.5 minutes in order to evaluate changes in technique. Our objective is to control a one gallon spill. The time for one gallon to drain through 1/4 inch tubing is 100 seconds which is within the allotted time span.

Test Nos. 3, 4, 5 and 12 in Table 1 show the results of volume scale-up from 1/2 pint to 1 quart of each component flowing through 1/4 inch tubing. The same volume was used in Test Nos. 4 and 5 to evaluate the effect of propellant container location. Control Test No. 12 produced what might be called a short look at the energy level to be expected from a one gallon spill.

Our air pollution control board permit allowed 1 quart maximum spills so the 1/4 inch tubing was changed to 1/8 inch orifices to lengthen the rundown time from 29 seconds to 65-75 seconds. This provides a 1 quart fire time that is similar to the time expected for a 1 gallon spill.

The propellant container location used in Control Test No. 14 produced a fire of acceptable intensity. This fire was a baseline for what we would expect without a suppressant.

The N_2O_4 monitor data was collected as a safety precaution to determine if stricter operating limits were required. The emissions were well dispersed within our boundaries. As might be expected, the more vigorous fires emit less N_2O_4 vapor than the ones with less intense reactions.

As quart quantities of propellant became more routinely used, the amount of suppressant required tended to cover the delivery tubes and hinder propellant flow. The propellant containers were elevated in Control Test No. 15 to eliminate this problem. It was necessary to move the containers so the propellant streams would hit the pan at about the same point as in Control Test No. 14. Slightly more mixing energy is obtained from the increased elevation. Increased distance between streams was not desirable because too much propellant drains away from the fire interface. The fire obtained in Control Test No. 18 was used as a new baseline for subsequent tests.

c. GELLED WATER HANDLING TECHNIQUES

1. Nozzle Design

The general goal was to create a wide heavy continuous sheet of polymer slurry. A nozzle that will deliver this type of pattern can be used for both propellant separation and general coverage. Several commercial nozzles appeared to come close to the desired performance. Commercial variations of these nozzles were tested. Some appeared to have possibilities if slightly modified. Pipes were flattened, nozzle orifices were enlarged, and entirely new nozzles were built in an effort to obtain an ideal spray pattern. The major designs are included in Table 2, most of these efforts resulted in either a flat stream that immediately converged into a narrow round stream or an irregular pattern unuseable for smooth coverage.

Evaluation of nozzles for use with ungelled formulations was much simpler. Performance information is usually available for water. The effect of the impact of the water spray on the gel was evaluated during fire tests.

2. Application Methods

The nozzles actually used in fire fighting tests are described as Fire Extinguishing Systems in Table 3. Although a few of the nozzles looked better than the Veejets in some tests, the versatility and dependability

of the Veejet is a major advantage. It could be pressure regulated to handle a wide range of gel viscosities. The spray could be varied from a fast covering fan to a well defined stream by controlling the pressure at the nozzle. The amount of pressure required was still reasonable with the stiffer gels.

Several of the other nozzles were evaluated for ungelled buffer delivery as part of a two stage extinguishing system. The impact from most of these nozzles caused fairly rapid deterioration of the first stage gel used to control the hypergolic reaction. Water fogs have been reported to be effective suppressants for A-50 fires (3). The very finely divided fog from a Hudson nozzle can be used without washing out the gel stage. Although the Hudson nozzle had the disadvantage of low deliverability for A-50 neutralization, it was effective in cutting off the air supply. After the fire is under control, additional gelled suppressant can be rapidly added to reduce the hazards from the A-50.

d. FIRE CONTROL AND PROPELLANT DEACTIVATION

1. Water Control Series

This series was included as a control representing present practices applied to our test set-up. In these tests and all the tests that involve flowing propellants, the propellants are allowed to run for 5 seconds before applying suppressant. This provides a well established fire. As indicated by the tests in Table 4, control of the hypergolic fire is possible if the water spray is used to separate the propellants. There was very dense fuming in every test. As observed in Test Nos. 3 and 4, low temperature does not reduce the fuming noted in Test Nos. 1 and 2. The use of the ungelled acetic acid-sodium acetate buffer in Test No. 4 gave no improvement.

Test No. 5 represents an attempt at controlling a sudden spill or dumping of one propellant followed by the other propellant. Although the fuel appeared to be washed away, there was a very large energy release when the N_2O_4 was dumped. It is known that explosions can occur at 90% water in A-50 (4). The results from Test No. 5 would indicate that water alone could create a false sense of security.

2. Gelled Water Systems - Flowing Spills

Evaluation of the suppressant system will include the following points:

- Consistency or gel concentration
- N_2O_4 scavenger concentration
- Temperature
- A-50 scavenger concentration
- Application technique

The evaluation of these points will be based upon the ability of the suppressant system to prevent reignition of the hypergolic reaction and to suppress the fuel-air fire.

The need for a stable gel is indicated in Test Nos. 1 and 2 of Table 5. Fresh water gels are immediately collapsed by the propellant and provide no more protection than water. Changing any component of the system usually changed the consistency. Therefore, a consistency factor measurement became a part of each test. Most of the tests were conducted with a buffer of one molar sodium acetate as the N_2O_4 scavenger and 1 molar acetic acid to neutralize A-50. The buffer capacity was tripled for Test No. 11 in hopes of improving N_2O_4 entrapment efficiency. The increased ionic strength of the buffer had an adverse effect on the gel quality. The excessive fuming appeared to be a result of the weaker gel. However, evaluation of higher gel concentration (Test Nos. 12 and 13 of Table 5) indicated the problem was the 3 molar buffer. The N_2O_4 was forming a solid reaction product at the higher buffer concentration. The solid caused excessive fuming by preventing N_2O_4 penetration into the gel. Low temperature (Gel Test No. 13) did not improve the fume control. Evidence of a solid by-product can be seen in the movies for Gel Test Nos. 12 and 13 at 65 seconds and 30 seconds respectively (See Appendix). The gel spray can be seen splashing over the blue color. Formation of a solid by-product was also noted in Gel Test No. 14 with a 2 molar buffer.

Difficulties continued with control of the air oxidized A-50 fire. Experience obtained from tests in the Water Control Series (see preceding section) suggested that water might be better for fire knock-down than gel. The following procedure was evaluated in Gel Series Test Nos. 6, 7, 8 and 9. The hypergolic reaction was stopped by using gel to separate the components. Additional gel may be used to prevent fuel and oxidizer run-off and to contain them for neutralization by the ungelled suppressant. The control obtained was not satisfactory. Fuming became heavier (especially from the N_2O_4), erosion of the gel separating the N_2O_4 and A-50 became a greater problem, and fire control was not appreciably better than with straight gel.

Temperature is known to be helpful in controlling propellant vaporization (5). Our laboratory tests indicated it would be a critical part of the suppressant system. Temperature was the major variable in Gel Series Test Nos. 17, 18 and 19. The warm suppressant (38°C) used in Test No. 18 appeared to add to the fire problem rather than control it. Although the fire was not as vigorous with the 18°C suppressant temperature used in Test 19, the control was very poor. At 16°C or below, the temperature of the suppressant does not appear to be so critical (Gel Series Test Nos. 10, 15 and 17). The temperature rise caused by the heats of solution and reaction of the various components of the system can also cause severe problems. These problems will be discussed as they arise.

The effect of temperature on the flow characteristics of the gelled suppressant should also be considered. The gel becomes stiffer at elevated temperature (see Figure 17). Increasing temperature caused handling problems with some of the gel systems. In order to improve the strength

of the gel noted in Gel Series Test No. 19, the concentration of polymer was increased to the maximum that could be pumped for Gel Test No. 20. The higher temperature of Gel Test No. 22 made this concentration too viscous to handle. Although the effect of temperature is reversible (see Table 6 for time, temperature, and quality data), agitation problems in a gelled system make rapid temperature changes difficult.

In some of the previous tests, it appeared that large quantities of gelled suppressant could build up in front of the propellant delivery tubes. Beginning with Gel Series Test No. 16 the propellant containers were elevated to eliminate the possibility of obstruction. In an actual crash situation such a blocking technique may be quite desirable. Since blockage may not be possible, techniques should be developed to control the worst situation.

Ideal neutralization would require thorough blending of stoichiometric quantities of propellant and suppressant. However, mixing the gel and propellants after delivery would not be possible in the envisioned emergency situation. Continual addition of a small stream of suppressant to the incoming propellant should provide some mixing and improve neutralization. The use of this technique was begun in Gel Series Test No. 17. Although there may have been a little improvement, there was no major change between this test and Gel Series Test Nos. 10 and 15.

In another attempt at control of the A-50 in air fire, Test Nos. 21, 22, and 23 were conducted using a low viscosity gel for the second stage. It was believed that the low viscosity stage could be used for improved fire knock-down properties without as much erosion of the separating dam as previously occurred with the ungelled buffer. This technique did not provide any major improvement in control.

The air oxidized A-50 fire remained the major problem. This fire was similar to air oxidized fires of ordinary fuel such as gasoline. Accepted methods of fighting this type of fire include foam and fog suppressants. Because of the low density of foam and fog, delivery of large amounts of neutralizers to the propellants was considered an obstacle. The necessity for evaluating these techniques became obvious during the terminal screening for the Demonstration Series. Fog was chosen because it would not have the compatibility problems with the buffer that a foaming agent might have.

A fog was used effectively in Test Nos. 28 and 29 of Table 5. The initial separation and coverage by the viscous gel was adequate. Concentration of N_2O_4 far exceeds the acetate buffer capacity in localized areas. This can be seen by the appearance of the blue color around the N_2O_4. The N_2O_4 boiling through at the end was probably caused by the high heat of reaction of excess N_2O_4 with formaldehyde. The N_2O_4 which spattered over the gel was responsible for most of the reignition problems.

Two A-50 scavengers were field tested. It was believed that these materials, being more specific for A-50, would improve toxicity control and fire suppression. Rapid formation of solid reaction products eliminated 2-4 pentanedione. The solid surface accentuated the already serious problem of A-50's tendency to flow across the suppressant surface (see Test No. 16 in Table 5). Formaldehyde forms a solid reaction product more slowly. This reaction product did not seem to cause a problem so formaldehyde was included in most of the tests until after the fog tests were conducted.

3. Control of Sudden Spills

This section also deals with gelled water systems. The results desired and the control used are a little different from the approach used for the flowing spills. One propellant is dumped from an open reservoir to simulate a sudden large rupture in a tank or a similar sudden spill. An attempt is made to neutralize this propellant and then the neutralization is checked by dumping the other propellant on top of the first spill.

After the nature of a sequential spill was observed in Test Nos. 24 and 25 of Table 5A, the minimum amount of gelled suppressant necessary to cover the spill was determined. Approximately 7 quarts was required to cover one quart of spilled propellant. The same quantity was used for control tests with water.

The minimum suppressant was used to show that the hazard is greatly reduced when using a gelled suppressant. None of the tests contained in Table 5A resulted in a detonation approaching the one that occurred in the Water Control Series (Test No. 5 of Table 4). In the Water Control Test, at least 23 seconds elapsed between the A-50 spill and the N_2O_4 spill. The only test with a gelled suppressant that had more neutralization time was Test No. 26 in Table 5A. The results of Test 26 should be discarded as invalid because the suppressant formulation was unuseable.

The effect of N_2O_4 spilling first, followed by A-50 was checked in Test No. 25 of Table 5A. No unusual results were observed.

Ideally, adequate amounts of any suppressant would be used and additional suppressant would be applied to subsequent spills for fume and toxicity control. However, an accurate estimate of the volume spilled may not be possible and a severe explosion could result if insufficient water were used.

4. Terminal Screening and Demonstration

The Demonstration Series originally planned for Table 7 was to have been a set of five tests summarizing the results of the program and the associated rehearsals necessary to establish proper timing. However, minor changes in technique and formulation did not provide the desired

improvement. In order to check the possibility that formaldehyde might be contributing to the problem, a complete practice series was conducted without formaldehyde. No obvious differences were observed, although minor variations in application technique may have masked the results. Firmer evidence that formaldehyde contributes to the problem was later obtained in Tests 28 and 29 of Table 5.

The technique used in both Test 5C and 5D of Table 7 was to establish separation of A-50 and N_2O_4 with a fairly stiff gel. The same gel was used to establish substantial N_2O_4 cover to absorb the continuing flow. Very little of the stiffer gel was allowed under the A-50. This was followed by a very low viscosity gel for control of the A-50. The technique with the less viscous gel was to use a combination of fairly hard sprays for fire knock-down followed by a smaller volume for continual neutralization.

Our best application technique using an all gel system, with or without formaldehyde, did not provide the desired control. It was decided to attempt development of an entirely different control method and expand the demonstration series for the additional rehearsals.

In addition to fog, a dry chemical extinguisher was also tested. The effect of dry chemical control for the A-50 in air fire can be seen in Test No. 7 of Table 7. The carbonate reacts with the buffer and N_2O_4 spattering oxidizer into the fuel. An untreated water fog was also tested on this spill. The spattering from the dry chemical residue continued to cause problems.

A fog cover for air exclusion was the final choice for control of the A-50 in air fire. Ungelled buffer rather than water was the base liquid for the fog. Although the fog volume was insufficient to neutralize a significant quantity of propellant, the buffered fog appeared to provide faster control. This could be a result of the composition of the blend of the fog and A-50 vapors. Hydrazine hydrate produced from a water fog could remain flammable. The buffered fog would produce a non-flammable solid of hydrazine acetate. Reignition had occurred in the fog Tests 28 and 29 of Table 5 but new laboratory information indicated the heat from the formaldehyde reaction with N_2O_4 could be responsible. In the localized areas of spent sodium acetate the heat from reacting formaldehyde could easily produce the boiling and sputtering that caused reignition. A formaldehyde free system with acetic acid-acetate buffered fog control of the fuel-air fire was evaluated in Test No. 6 of Table 7. This system provided the best control obtained for the flowing spill. A successful repeat run was conducted with the spill labeled Rehearsal Test No. 5 of Table 7.

The actual demonstration, labeled simply Test Nos. 1-5, was conducted with the wind direction occasionally placing the fire fighter in an unfavorable position. Fuming obstructed his view and interferred with his placement of the suppressant. The mobility of the prototype system should eliminate this problem. The best summary of the program can be seen in the spills labeled Rehearsal Test Nos. 1-5 of Table 7.

CONCLUSIONS

This system should reduce the hazards arising from spills of N_2O_4 and Aerozine-50. The study has shown that:

A gelled suppressant can be delivered to an hypergolic fire and will prevent further hypergolic reaction.

A finely dispersed fog will stop the fuel in air fire without destroying the gelled dam.

The acetic acid-sodium acetate buffer is necessary to neutralize the N_2O_4 and to prevent gel collapse due to high acidity.

The heat of reaction of formaldehyde with N_2O_4 makes control more difficult.

The formation of solid reaction products will interfere with neutralization of additional propellant. (Solidifying could be an advantage if it were possible to contact all of the propellants.)

The temperature of the gelled suppressant is critical to success. Effective control becomes impossible if the temperature of the gelled suppressant is above 16°C.

In the event of LES initiation, it may be necessary to fight a fire with portable equipment adapted to helicopter delivery. This would limit the amount of suppressant available. Therefore, a gel block that keeps hypergolic propellant apart has definite advantages over an ungelled suppressant that depends upon constant flow for propellant separation.

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APPENDIX A

List of Tables

TABLE 1

CONTROL SERIES - SCALE UP AND UNCONTROLLED FIRES

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Rundown Time(sec.)	Propellant Container Location	N_2O_4 Monitor Distance (ft)	N_2O_4 Monitor Concentration (Max. ppm)	Remarks
A*	--	--	250	-0-	Spill	Figure 2	--	--	Brown plume dissipates within plant boundary.
B*	--	--	450	-0-	Spill	Figure 2	400	Nil	Increased fume density - dissipated well within plant boundary.
1	27	23	225	225	Simultaneous Spill	Figure 2	345	Nil	Loud detonation 220 milliseconds after the spill. An extinguisher cannot be used during a spill of this type.
2	20	22	225	225	9	Figure 3	210	Nil	A very small fire. Total fire time was about 30 seconds.
2(a)*	19	27	500	-0-	17	Figure 3	150	Nil	The N_2O_4 monitor was not in the center of the plume.
3	18	7	225	225	9	Figure 3	50	30	Rerun of No. 2 with pan slant adjusted. Fire was about the same.
4	19	13	450	450	16	Figure 3	50	20	The larger quantity initially caused more vigorous mixing resulting in a small explosion. The following fire was about the same as No. 3.
5	19	13	450	450	16	Figure 4	--	--	N_2O_4 had been running away from A-50. Location change gives better interface and fire.

TABLE 1 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Rundown Time (sec.)	Container Location	N_2O_4 Monitor Distance (ft)	N_2O_4 Monitor Concentration (Max. ppm)	Remarks
6	22	10	450	450**	16	Figure 4	--	--	More vigorous fires were expected from prior work with N_2H_4. This test indicated the fuel is not the problem.
7*	21	13	450	450	16	Figure 5	35	75	After an initial detonation, the fire continued at an intensity only slightly above No. 5.
8*	22	13	450	450	16	Figure 6	50	Nil	Four severe detonations during propellant flow. It will be rerun because of flow system malfunction.
9	28	13	450	450	16	Figure 6	50	10	A series of 4 double detonations occurred during rundown followed by a small fire. Total time was 32 seconds.
10	29	17	450	450	16	Figure 7	50	Nil	Five or six detonations occurred during rundown. Most of them were severe. A small fire followed. Figure 7 produces the most violent flow conditions tested.
11	23	14	940	940	75	Figure 8	--	--	First test made with 1/8 inch orifices. A good fire until the heat caused propellant delivery problems.
12	18	6	940	940	29	Figure 9	150	5	A good fire during propellant flow with four small detonations. The increase in intensity was no more than expected from doubling the volumes.

TABLE 1 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Rundown Time(sec.)	Container Location	N_2O_4 Monitor Distance (ft)	N_2O_4 Monitor Concentration (Max. ppm)	Remarks
13	26	11	940	940	75	Figure 10	150	5	The rundown with 1/8 inch orifices is more than twice as long as with 1/4 inch causing more heat buildup on the delivery tube. Moving the containers back does not entirely prevent N_2O_4 vaporization.
14	25	24	940	940	75	Figure 10	--	--	Heat shields added to the delivery tubes make the heat buildup acceptable. It will be no problem when testing extinguishers. There is a vigorous fire during the entire rundown.
15	8	12	470	470	38	Figure 11	--	--	Propellant mixing was insufficient during rundown. Excessive fuming afterwards.
16	9	12	470	470	40	Figure 12	--	--	Fire intensity is insufficient.
17	10	14	235	235	20	Figure 13	--	--	Additional container elevation mixes the propellants a little better. The intensity is still a little low.
18	9	15	470	470	35	Figure 14	--	--	The fire intensity is equal to or higher than that obtained from the conditions in Control Tests 13 and 14.

Notes:

* No movies were made of this test.

** Hydrazine alone was used as the fuel in this test.

TABLE 2

NOZZLE PERFORMANCE WITH SOLUTIONS OF GELGARD® M POLYACRYLAMIDE

Nozzle	Formulation(1)	ΔP (psi)	Max. Range (ft.)	Rate (gpm)	Remarks
Rex Flatspray	Water	5	7	4.0	This nozzle provides a fairly narrow spray which allows extinguishant to be delivered with some precision.
Rex Flatspray	Water	10	10	5.5	
Rex Flatspray	Water	15	12	6.8	
Rex Flatspray	I	12	5	--	Insufficient pressure to obtain spray pattern.
Rex Flatspray	I	15	7	--	Poor spray pattern.
Rex Flatspray	I	20	9	4.3	The spray pattern is a little uneven.
Rex Flatspray	D	20	9	4.0	The spray pattern is a little uneven.
Rex Flatspray	G	35	6	--	Poor coverage.
Hardy Dual Nozzle	Water	5	12	2.2	Good range combined with spray versatility for coverage.
	Water	10	16	2.3	
Hardy Dual Nozzle	I	20	16	2.1	The gel inhibits break-up, which improves range, but spray deteriorates.
	I	30	21	--	
Hardy Dual Nozzle	G	25	7	1.3	
	G	35	17	--	
1/2" x 3" Pipe Nipple	G	50	9	20.	A good stream for fuel separation.
	G	60	11	--	Good coverage is possible by hand manipulation; however, control is not dependable.

Note:

(1) See Table 8 for the formulation used.

TABLE 2 (cont.)

Nozzle	Formulation(1)	ΔP (psi)	Max. Range (ft.)	Rate (gpm)	Remarks
1/4 Circle	G	20	5	--	Spray is too coarse.
Lawn Spray	G	30	12	--	Pattern is too broad for application.
Ross	G	60	--	--	Useable for both separation and coverage.
No. 11	G	80	10	7.5	Very good for both separation and coverage.
1-1/2" Fire Nozzle	G	75	--	--	The gel quickly loads up the dispersing plate and destroys the pattern.
1/16" x 3"	G	40	--	--	A 3-inch wide flat stream.
VeeSlot	G	75	12	17	Stream breaks up but covers fairly well.
	G*	75	--	--	Stream break-up is worse.
1/16" x 12"	G	50	1	--	Stream converges, poor coverage.
VeeSlot	G	90	4	--	Stream converges, poor coverage.
3/4" Veejet	G	30	10	--	Stream converges.
No. U80400	G	40	14	--	Broad coverage but a fairly coarse spray.
No. U80400	G	50	--	--	Fair coverage.
on a	G	55	14	13	Broad coverage with good build-up.
1" x 3'	N	65	--	--	Stream converges--higher viscosity requires higher pressure.
wand	N	75	--	--	Very good coverage and build-up.
3/4" Veejet	N	65	--	--	Stream converges.
No. U50400 on a 1" x 3' wand	N	75	--	--	Same as Veejet No. U80400 except tighter pattern (50° vs. 80° spray nozzle).

*0.2% MGL (water soluble polymer) added for one test.

TABLE 3

FIRE EXTINGUISHING SYSTEMS

Delivery System	Nozzle	Application Technique	Remarks
a-1 a-2	3/4" Veejet No. U50400	Propellant separation with nozzle vertical. General coverage with nozzle horizontal.	A hard non-drifting water spray that provides a coarse fairly wide (50°) non-converging heavy pattern with gel.
b	Rex Flatspray	Separation, vertically-coverage, horizontally.	This is a smoother water spray but gel spray is not even enough for good coverage.
c	Heavy Duty Garden Hose Nozzle	A cone spray pattern was used for coverage and separation.	This represents a scale-down of the fire hose nozzle used at KSC. It cannot be used for GELGARD® M polymer.
d	Hardy Dual Nozzle	Round stream for dam building - flat spray for coverage.	The water pattern is good. The gel spray is much too thin and irregular for coverage.
e	1/2" x 3" Pipe Nipple	Heavy round stream for dam building. Hand flatten spray for coverage.	Good separation - poor control for general coverage.
f-1 f-2	Ross No. 11	Separation, vertically. Coverage, horizontally.	A perforated plate, multiple stream nozzle that may provide good coverage and separation. However, the nozzle plugs easily and the spray does not carry dependably.

TABLE 3 (cont.)

Delivery System	Nozzle	Application Technique	Remarks
g	3/8" Flatjet No. P4050	General fuel coverage.	Used for ungelled buffer in conjunction with a Veejet for dam building.
h	Pressurized 2-1/2 gal. water extinguisher.	General fuel coverage.	Used for ungelled buffer in conjunction with a Veejet for gel delivery.
i	Hudson Fog Nozzle	General fuel coverage.	Used for fog delivery of ungelled fluids to stop the A-50 in air fire. The fog does not disrupt the gel.
j	Ansul 20-D Dry Chemical Extinguisher	General fuel coverage.	Another attempt at shutting off the air supply to the A-50.
k	2-Hudson Fog Nozzles	General fuel coverage.	Two nozzles were spaced 16 inches apart to help prevent the A-50 fire from moving around the edge of the fog cone.

TABLE 4

WATER CONTROL SERIES

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation[1]	Suppressant Delivery System[2]	Suppressant Ratio to A-50	Suppressant Temp. °C	Suppressant Delivery Time (sec)	Suppressant Delivery ΔP (psi)	Remarks
1	18	16	450	450	Figure 4	Water	a-2	59:1	9	20	25	Dense fumes during 15 sec. propellant run.
2	16	19	940	940	Figure 10	Water	b	23:1	29	65	10	Dense fumes during propellant run. Immediate reignition if water is moved.
3	9	16	940	940	Figure 14	Water	c	15:1	1	70	35	Low temperature water does not alleviate fuming.
4	6	11	940	940	Figure 14	A	c	17:1	-5	65	50	Ungelled buffer is no better than water.
5[3]	8	13	940	940	Figure 15	Water	c	7:1	11	17	80	Heavy detonation occurred within 0.3-0.4 seconds after N_2O_4 spill-dense fuming.

Notes:

(1) See Table 8 for formulations used.

(2) The application techniques and nozzles used are described in Table 3.

(3) Sequential spill of A-50, covered with water and followed by N_2O_4 spill.

TABLE 5

GELGARD® M POLYACRYLAMIDE SERIES

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation[1]	Suppressant Delivery System[2]	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
1	17	19	470	470	Fig. 10	D	b	18:1	19	Unbuffered gel is collapsed by propellant, allows reignition.
2	18	20	470	470	Fig. 10	D	d	10:1	19	This nozzle allows more precise separation but unbuffered gel is no better than water.
3	17	18	470	470	Fig. 10[3]	G	e	40:1	16	Buffer prevents propellant from collapsing gel. The fire continued on either side of the gel.
4	13	10	470	470	Fig. 10	G	f	--	--	Nozzle plugged.
4a	16	19	470	470	Fig. 10	G	f-1&2	40:1	18	Nozzle restricted flow. Dam formation for separation was slow. Coverage was also restricted.
5	13	12	470	470	Fig. 10	G	a-1&2	40:1	13	Separation and coverage completed within 10 seconds. Attempted to control reignition by additional coverage.
6	18	18	470	470	Fig. 10	G A	a-1 g	13:1 12:1	18 18	Separation is rapid but ungelled suppressant causes deterioration of the dam. Heavy fuming.
7	13	13	470	470	Fig. 10	G A	a-1 h	18:1 4:1	13 13	More gel used for separation, little N_2O_4 cover. Heavy fuming caused by ungelled buffer.

TABLE 5 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation[1]	Suppressant Delivery System[2]	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
8	14	16	470	470	Fig. 10	G A	a-1&2 h	26:1 6:1	16 14	More gel used for separation and cover. Good separation but heavy fuming and some fire problem remains.
9	16	16	940	940	Fig. 10	G A	a-1&2 f-2	16:1 16:1	16 16	Heavier use of ungelled buffer causes more fuming. Separation by gel good, but ungelled buffer causes some deterioration.
10[4]	19	17	940	940	Fig. 10	G	a-1&2	17:1	16	Gelled suppressant traps the propellant and reduces the fuming better than ungelled suppressant.
11	13	17	940	940	Fig. 10[5]	K	a-1&2	33:1	13	Increased buffer capacity weakened gel. More suppressant used in an attempt to prevent mixing of propellants.
12	14	18	940	940	Fig. 10	L	a-1&2	34:1	18	Gel still too thin for good separation. Temperature could be contributing to fuming. Blue solid reaction product formed with N_2O_4.
13	15	17	940	940	Fig. 10	M	a-1&2	33:1	5	Good separation but fire problem as bad or worse than before. Both N_2O_4 and A-50 are on the gel surface.
14	13	17	940	940	Fig. 10	J	a-1&2	33:1	16	Lower buffer concentration did not improve control. Propellant penetration still bad.

TABLE 5 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation[1]	Suppressant Delivery System[2]	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
15	14	17	940	940	Fig. 10	G	a-1&2	32:1	16	No solid reaction products formed. Penetration better but fire and fume control is still poor.
16	14	16	940	940	Fig. 13	O	a-1&2	25:1	0	Including both A-50 detoxicant and low temperature did not give much improvement. White, solid reaction product formed with A-50. A-50 floated on the gel, reigniting easily.
17	7	14	940	940	Fig. 14	G	a-1&2	31:1	4	Continual addition of a small stream of suppressant to the propellants improves the control a little. Fire and fuming problems still exist.
18	8	13	940	940	Fig. 14	G	a-1&2	31:1	38	The warm suppressant offered almost no control and actually appeared to add to the fire problem.
19	12	14	940	940	Fig. 14	G	a-1&2	41:1	18	Although the suppressant did not add to the problem, control was poor. Gel was too weak for dam.
20	11	13	940	940	Fig. 14	V	a-1&2	30:1	-2	A-50 would not penetrate. Both the reaction product formed with formaldehyde and gel viscosity contributed to the problem.

TABLE 5 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation(1)	Suppressant Delivery System(2)	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
21	12	16	940	940	Fig. 14	Y F	a-1 a-2	16:1 20:1	2 0	Insufficient material for good separation. A-50 does not penetrate. Fire and fume problem is still bad.
22(4)	10	13	940	940	Fig. 14	V S	a-1 a-2	6:1 32:1	4 2	The gel intended for the dam was too viscous for delivery, but the less viscous gel stage appeared to have good fire knock-down properties.
23	6	12	940	940	Fig. 14	U S	a-1 a-2	8:1 26:1	4 -4	Delivery of thick gel was slow. Suppression with the less viscous gel appears to require more precise control. Overall performance was fair.
24-27		---- See Table 3A ----								
28	18	14	940	940	Fig. 14	T Water	a-1 i	27:1 1:1	6 21	Good separation and N_2O_4 coverage. Some sputtering through later in the test. The fire kept circling the fog delaying complete control.

TABLE 5 (cont.)

Test No.	Temp. °C Air	Fire Pan	Propellant N_2O_4 (cc)	A-50 (cc)	Container Location	Suppressant Formulation(1)	Delivery System(2)	Ratio to A-50	Temp. °C	Remarks
29	18	17	940	940	Fig. 14	T	a-1	17:1	7	The lower quantity of gel provided adequate separation and N_2O_4 coverage. The fog formed a dense white fume but control was no better than with the water fog. The fire could be extinguished but was reignited by sputtering.
						B	i	1:1	18	

Notes:

(1) See Table 8 for formulations used.

(2) The application techniques and nozzles are described in Table 3.

(3) The propellant containers were shifted 30 inches from the end of the pan for Test Nos. 3-15.

(4) No movies were made of this test.

(5) The propellant orifices were elevated 3 inches above the pan for this test.

TABLE 5A

GELGARD® M POLYACRYLAMIDE SERIES - SEQUENTIAL SPILLS[1]

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation	Suppressant Delivery System	Suppressant Ratio to A-50	Suppressant Temp. °C	Seconds Between Spills	Remarks
24	8	11	235	235	Fig. 15	S	a-2	32:1	2	23	Dense N_2O_4 boil-off but no fire nor detonations occurred.
25[2]	8	11	235	235	Fig. 15	S	a-2	22:1	4	11	No fire nor detonations occurred. There were white fumes afterwards produced by A-50 forming hydrates and acetates. The gel appears to wash away with the spill too easily.
26[3]	6	9	940	940	Fig. 15	X	a-2	--	6	110	Too viscous for effective delivery. Spread small amount in ropy strands. Small fires and minor detonations resulted.
27	8	11	940	940	Fig. 15	R	a-2	7:1	8	8	Gel stopped A-50 fume. N_2O_4 caused a little sputtering. Gel was a little thick for smooth coverage.

Notes:

(1) A-50 is spilled, then isolated and covered with suppressant, and immediately followed by the N_2O_4 spill.

(2) The spill order was reversed for Test No. 25. N_2O_4 was spilled and blanketed, then A-50 was spilled.

(3) Movies were not obtained for this test.

TABLE 6

TEMPERATURE DEPENDENCE OF
GELGARD® M POLYACRYLAMIDE FLOW CHARACTERISTICS

3.5% Polymer + 8.2% Sodium Acetate + 6% Acetic Acid + 10% 2-Butanone
Based on Total Weight as Water

Temperature (Degrees C)	Batch No.	Solution Age (hr.)	Gel Quality			
			Flow Index (sec./liter)		Slump (Tangent)	
			5 psi	10 psi	1 min.	5 min.
4	1	2	29.0	--	0.06	0.06
6	1	27	29.4	--	--	--
10	1	3	--	--	0.07	--
15	1	6	36.6	--	0.12	--
19	1	29	52.0	--	0.15	--
21	2	2	70.0	15.0	0.21	0.21
22	2	0.5	66.0	16.0	0.23	0.22

TABLE 7

DEMONSTRATION SERIES

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation(1)	Suppressant Delivery System(2)	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
1'(3)	14	17	940	940	Fig. 15(4)	Water	c	7:1	10	Time lapse between A-50 spill and N_2O_4 was 23 seconds. Severe detonation occurred 0.5 second after N_2O_4 spill. Heavy fuming.
2'	14	17	940	940	Fig. 15(4)	S	a-2	10:1	7	Time lapse between A-50 and N_2O_4 was 18 seconds. Heavy fuming but no fire nor detonations.
5'	13	16	940	940	Fig. 14	X S	a-1 a-2	16:1 27:1	4 7	Handling characteristics of the dam were excellent. A-50 would not penetrate the gel used for general control. Fire and fume problem still exists.
5A	17	19	940	940	Fig. 14	X Q	a-1 a-2	18:1 16:1	0 2	The viscosity of the control gel was not lowered sufficiently for A-50 penetration.
5B	17	21	940	940	Fig. 14	X P	a-1 a-2	26:1 16:1	-2 3	Handling characteristics of the dam remain excellent. A-50 burns in the control stream. It is more a fuel floating problem than a penetration problem.

TABLE 7 (cont.)

Test No.	Temp. °C Air	Fire Pan	Propellant N_2O_4 (cc)	A-50 (cc)	Container Location	Suppressant Formulation[1]	Delivery System[2]	Ratio to A-50	Temp. °C	Remarks
2A	22	18	940	940	Fig. 15[4]	H	a-2	5:1	11	Insufficient gel was used to establish a complete cover. This resulted in a little fire but no detonations.
5C	22	20	940	940	Fig. 14	H E	a-1 a-2	26:1 14:1	11 8	Good initial separation. Some fire and fuming continued. A-50 penetration of a less viscous gel is still poor.
1A	24	16	940	940	Fig. 15[4]	Water	c	7:1	6	Time lapse between A-50 spill and N_2O_4 was 23 seconds. A spectacular detonation occurred 0.29 seconds after N_2O_4 spill.
2C[5]	24	17	940	940	Fig. 15[4]	H	a-2	9:1	6	Twenty seconds elapsed between spills. Gel was too stiff for even coverage. Fire in many pockets.
3A	25	16	940	940	Fig. 14	None---Control Fire---				The propellant provided a vigorous fire during the 68 second rundown time. Intensity decreased at the end of 75 seconds.
4A	25	14	940	940	Fig. 14	Water	c	21:1	7	Dense fuming made it difficult to see fire reignite when water was moved.
5D	25	14	940	940	Fig. 14	H E	a-1 a-2	26:1 24:1	9 9	Good initial separation but A-50 in air fire could not be kept down.

TABLE 7 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation[1]	Suppressant Delivery System[2]	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
6	24	18	940	940	Fig. 14	H A	a-1 i	18:1 1:1	13 4[6]	Good separation by the gel and excellent fire control from the acetic acid-acetate fog.
7	24	18	940	940	Fig. 14	H W	a-1 j	17:1 --	16 --	Good separation by the gel but the dry chemical control reacts with the buffer causing oxidizer to spatter into the fuel.
Reh. 1	18	17	940	940	Fig. 15[4]	Water	c	7:1	21	The time between A-50 and N_2O_4 spills was 24 seconds. Severe detonation occurred 0.33 seconds after N_2O_4 spill.
Reh. 2	18	18	940	940	Fig. 15[4]	E	a-2	7:1	2	The time between A-50 and N_2O_4 spills was 10 seconds. There was a little sputtering but no detonation nor fire. The N_2O_4 boil-off was shorter and less dense than the boil-off in rehearsal test no. 1.
Reh. 3	18	18	940	940	Fig. 14	None	--	Control Fire	--	A vigorous uncontrolled fire. The propellant rundown time was 65 seconds.
Reh. 4	18	18	940	940	Fig. 14	Water	c	24:1	21	Dense fuming--hypergolic fire restarts immediately if water is moved.

TABLE 7 (cont.)

Test No.	Temp. °C Air	Fire Pan	Propellant N_2O_4 (cc)	A-50 (cc)	Container Location	Suppressant Formulation[1]	Delivery System[2]	Ratio to A-50	Temp. °C	Remarks
Reh. 5	19	19	940	940	Fig. 14	H	a-1	22:1	2	Good propellant separation.
						A	k	2:1	7	Fair N_2O_4 fume control. Good A-50 fire control (white fumes are hydrazine acetate).
1	18	9	940	940	Fig. 15[4]	Water	c	7:1	18	The time between A-50 and N_2O_4 spills was 23 seconds. A spectacular detonation occurred 0.5 seconds after the N_2O_4 spill.
2	18	10	940	940	Fig. 15[4]	E	a-2	9:1	3	The time between A-50 and N_2O_4 spills was 9 seconds. There was no detonation but there was some fire. The lapsed time may be inadequate for neutralization. Previously control was obtained at 18 seconds.
3	17	10	940	940	Fig. 14	None -- Control Fire --				The uncontrolled flowing spill provided a very vigorous fire with audible popping.
4	17	15	940	940	Fig. 14	Water	c	26:1	18	Dense fuming while water is separating components. Hypergolic fire restarts immediately if water is stopped.

TABLE 7 (cont.)

Test No.	Temp. °C Air	Temp. °C Fire Pan	Propellant N_2O_4 (cc)	Propellant A-50 (cc)	Propellant Container Location	Suppressant Formulation(1)	Suppressant Delivery System(2)	Suppressant Ratio to A-50	Suppressant Temp. °C	Remarks
5	17	14	940	940	Fig. 14	H A	a-1 k	20:1 2:1	3 7	Good propellant separation. Unusual wind direction caused fumes to block the fire fighter's view. This resulted in poor fog placement and poor control except the once or twice when the view was clear.

Notes:

(1) See Table 8 for formulations used.

(2) See Table 3 for delivery system used.

(3) The movie titles for 1', 2' and 5' do not have the prime mark. Please see the film catalogue in the Appendix for the reel number to avoid confusion between practice runs and the final demonstration.

(4) A sequential spill--the A-50 is spilled, covered by suppressant, and then N_2O_4 is spilled.

(5) No Test No. 2B was conducted.

(6) Although temperature is given for base liquid in fog system, the delivered temperature depends upon the weather.

TABLE 8

FIRE SUPPRESSANT FORMULATIONS

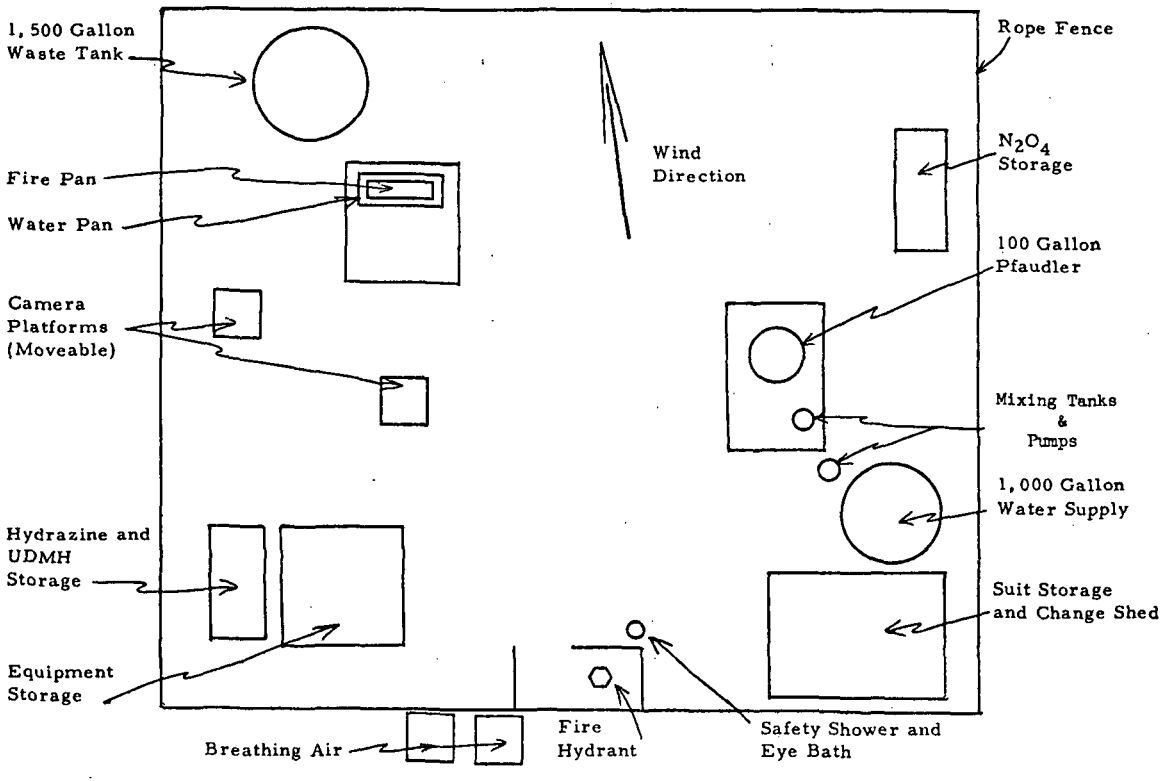
Formulation	Concentration (Based on Total Weight as Water)				Gel Quality			
					Flow Index (sec./liter)		Slump (Tangent)	
	Polymer	Sodium Acetate	Acetic Acid	Aerozine-50 Detoxicant	5 psi	10 psi	1 min.	5 min.
A	---	8.2%	6%	--	--	--	--	--
B	---	8.2%	6%	6% Formaldehyde	--	--	--	--
C	3% Norbak	8.2%	6%	--	50	12	0.12	0.12
D	0.3% GELGARD® M	--	--	--	30	--	0.096	0.071
E	3.0% GELGARD® M	8.2%	6%	--	--	30	--	--
F	3.25% GELGARD® M	8.2%	6%	--	--	48	0.20	0.19
G	3.5% GELGARD® M	8.2%	6%	--	--	105	0.33	0.33
H	3.7% GELGARD® M	8.2%	6%	--	--	235	0.37	0.37
I	3.5% GELGARD® M	8.2%	6%	10% 2-Butanone	37	--	0.12	--
J	3.75% GELGARD® M	16.4%	12%	--	--	--	--	--
K	3.5% GELGARD® M	24.6%	18%	--	--	55	0.18	0.18
L	3.75% GELGARD® M	24.6%	18%	--	--	105	0.21	0.2
M	3.9% GELGARD® M	24.6%	18%	--	--	--	--	--
N	4.0% GELGARD® M	24.6%	18%	--	--	--	0.44	0.44
O	3.75% GELGARD® M	8.2%	6%	8% 2-4 Pentanedione	106	30	0.19	0.17
P	3.0% GELGARD® M	8.2%	6%	6% Formaldehyde	--	28	--	--
Q	3.25% GELGARD® M	8.2%	6%	6% Formaldehyde	--	41	0.18	0.16
R	3.5% GELGARD® M	8.2%	6%	6% Formaldehyde	--	55	0.32	--
S	3.4% GELGARD® M	8.2%	6%	6% Formaldehyde	--	47	--	--
T	3.85% GELGARD® M	8.2%	6%	6% Formaldehyde	--	290	--	--
U	4.1% GELGARD® M	8.2%	6%	6% Formaldehyde	--	550	--	--
V	4.3% GELGARD® M	8.2%	6%	6% Formaldehyde	--	--	0.38	0.38
W	Ansul Dry Chemical Extinguisher							
X	3.9% GELGARD® M	8.2%	6%	6% Formaldehyde	--	340	--	--
Y	3.75% GELGARD® M	8.2%	6%	--	--	--	--	--

APPENDIX B

List of Figures

FIGURE 1

TEST SITE AND EQUIPMENT ARRANGEMENT



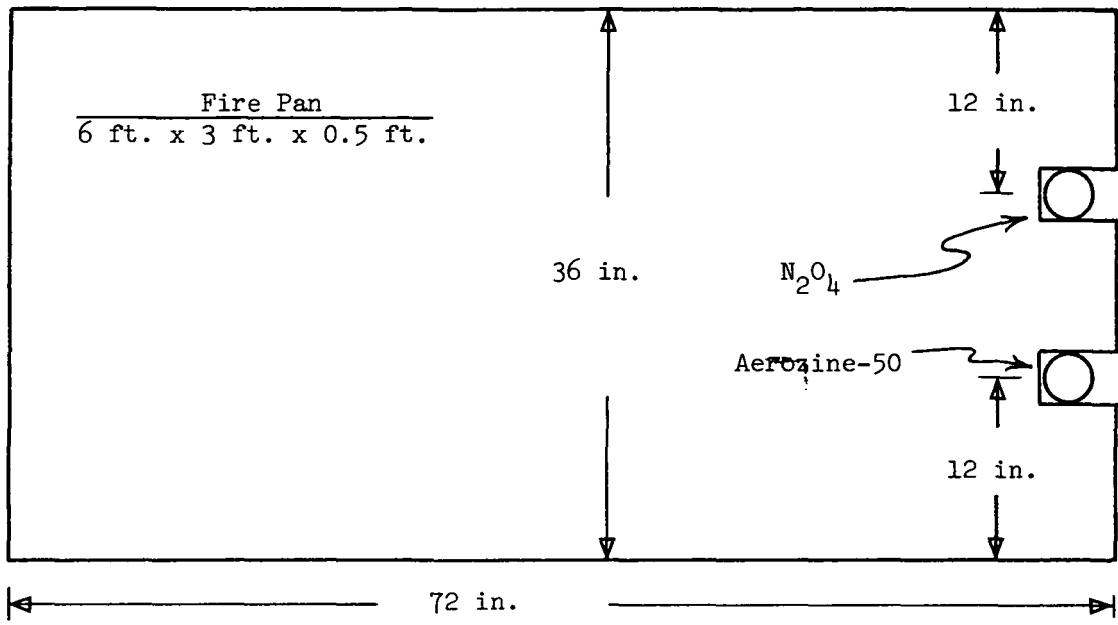


Figure 2: Sudden Simultaneous Spill
First Location of Propellant Containers

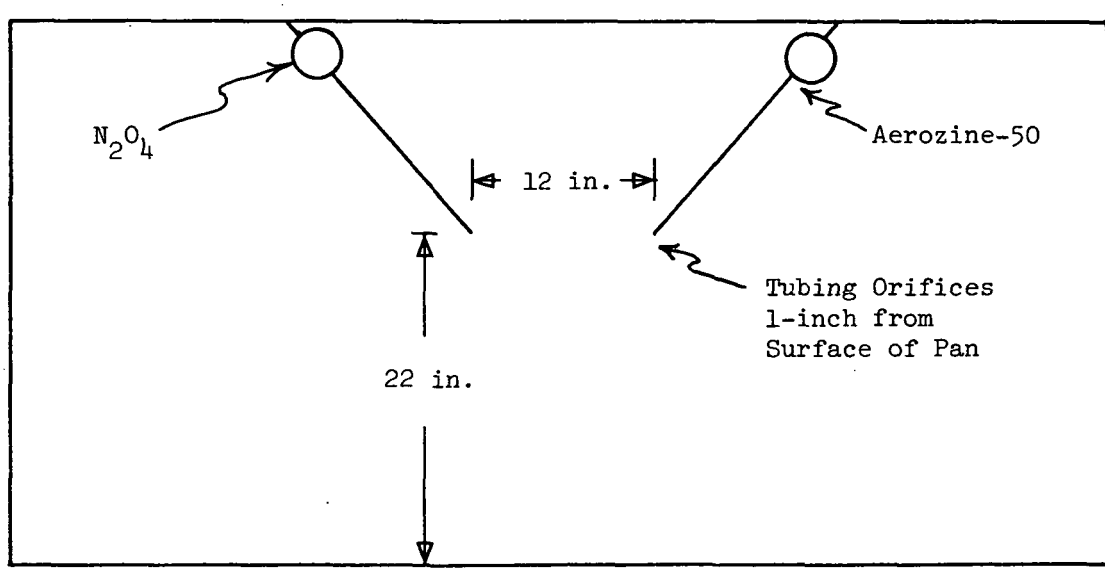


Figure 3: Flowing Spill Through 1/4 Inch I.D. Tubing
Second Location of Propellant Containers

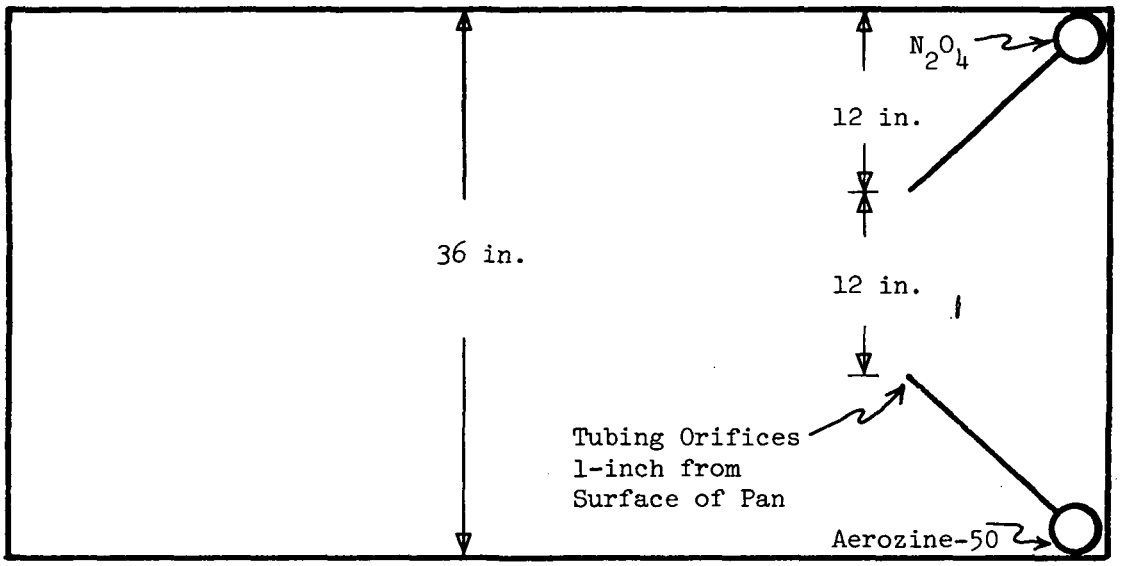


Figure 4: Flowing Spill Through 1/4 Inch I.D. Tubing
Third Location of Propellant Containers

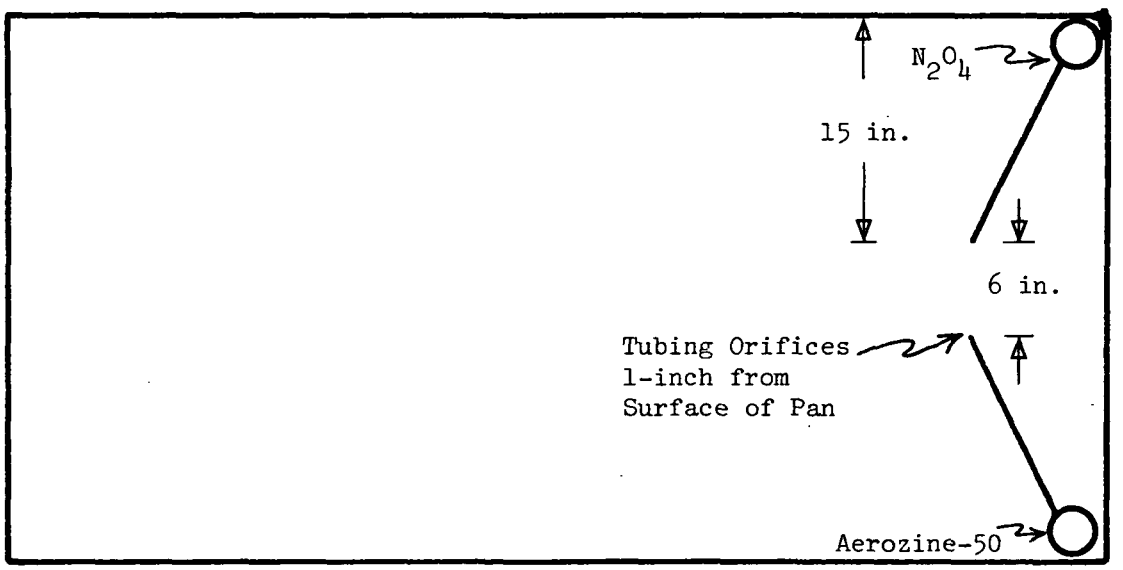


Figure 5: Flowing Spill Through 1/4 Inch I.D. Tubing
Fourth Location of Propellant Containers

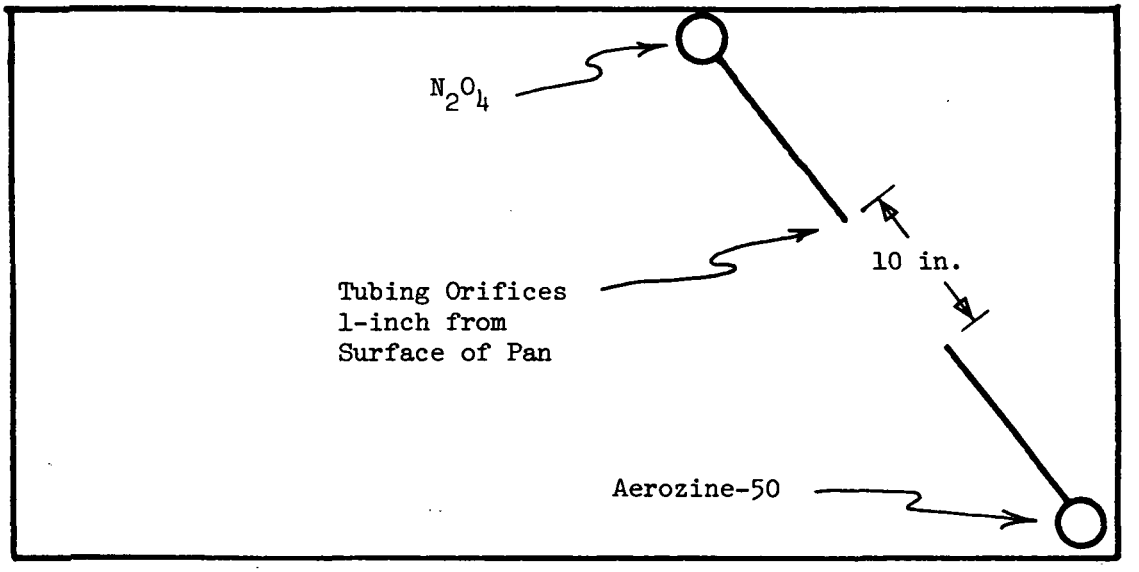


Figure 6: Flowing Spill Through 1/4 Inch I.D. Tubing
Fifth Location of Propellant Containers

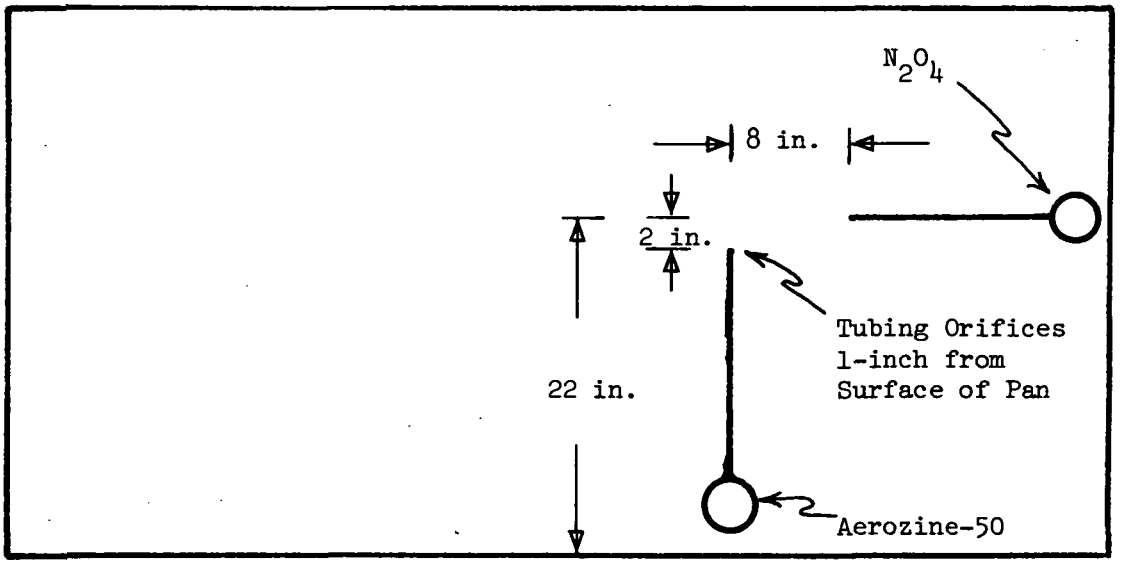


Figure 7: Flowing Spill Through 1/4 Inch I.D. Tubing
Sixth Location of Propellant Containers

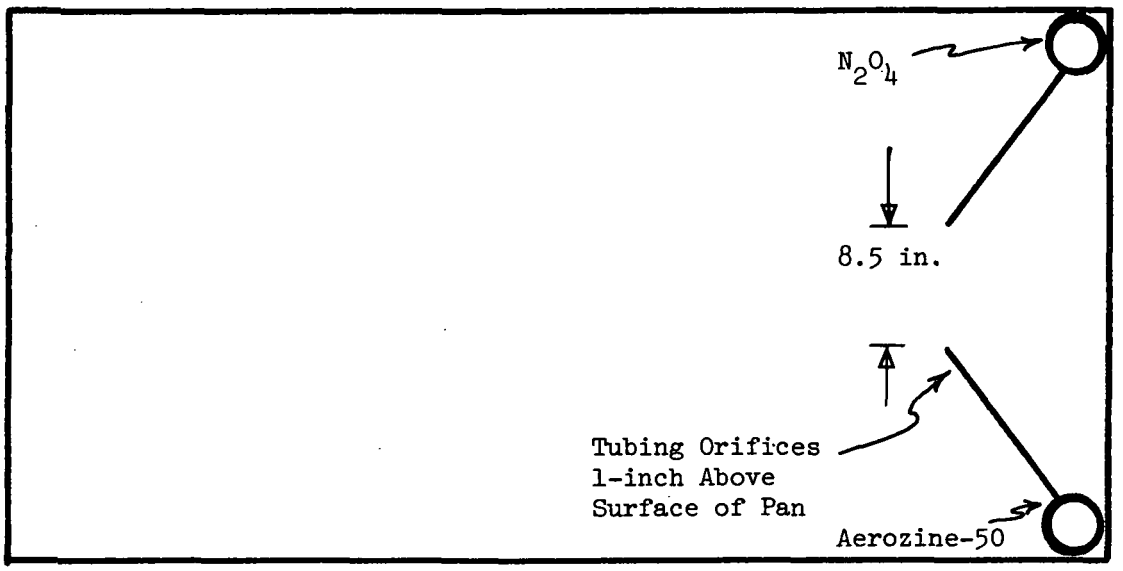


Figure 8: Flowing Spill Through 1/8 Inch Orifices
Seventh Location of Propellant Containers

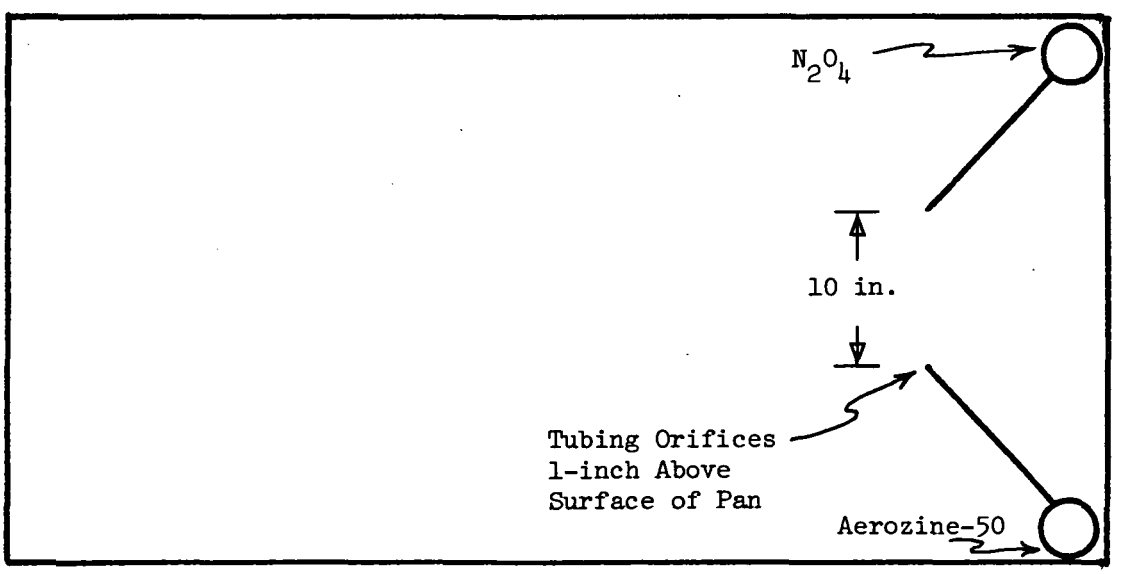


Figure 9: Flowing Spill Through 1/4 Inch Orifices
Eighth Location of Propellant Containers

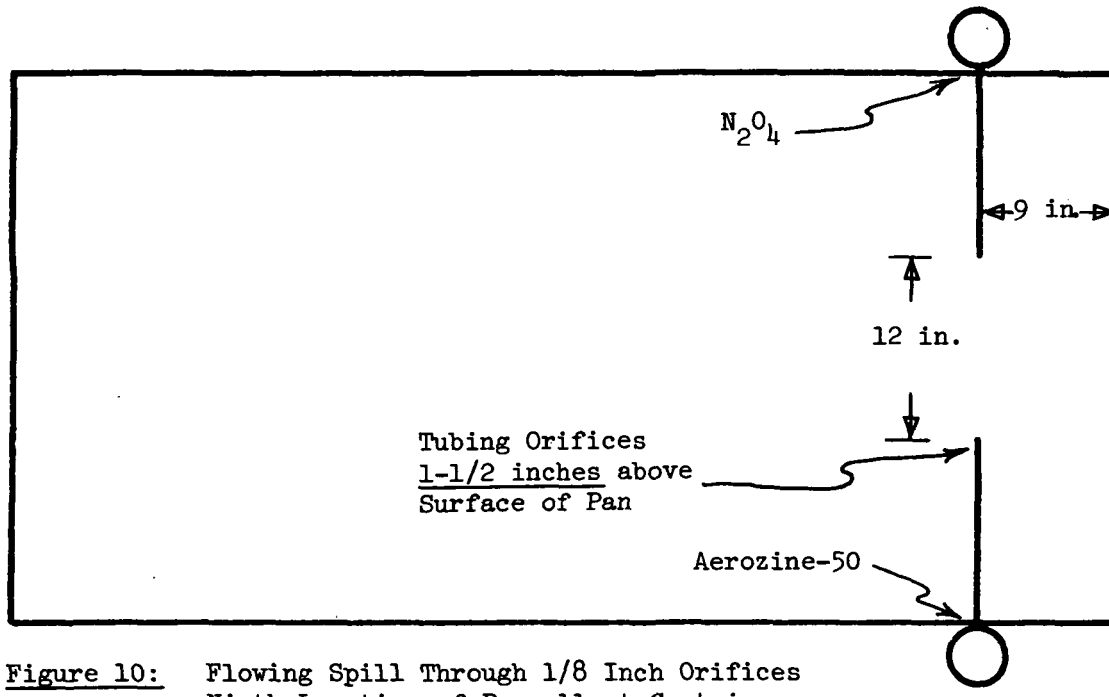


Figure 10: Flowing Spill Through 1/8 Inch Orifices
Ninth Location of Propellant Containers

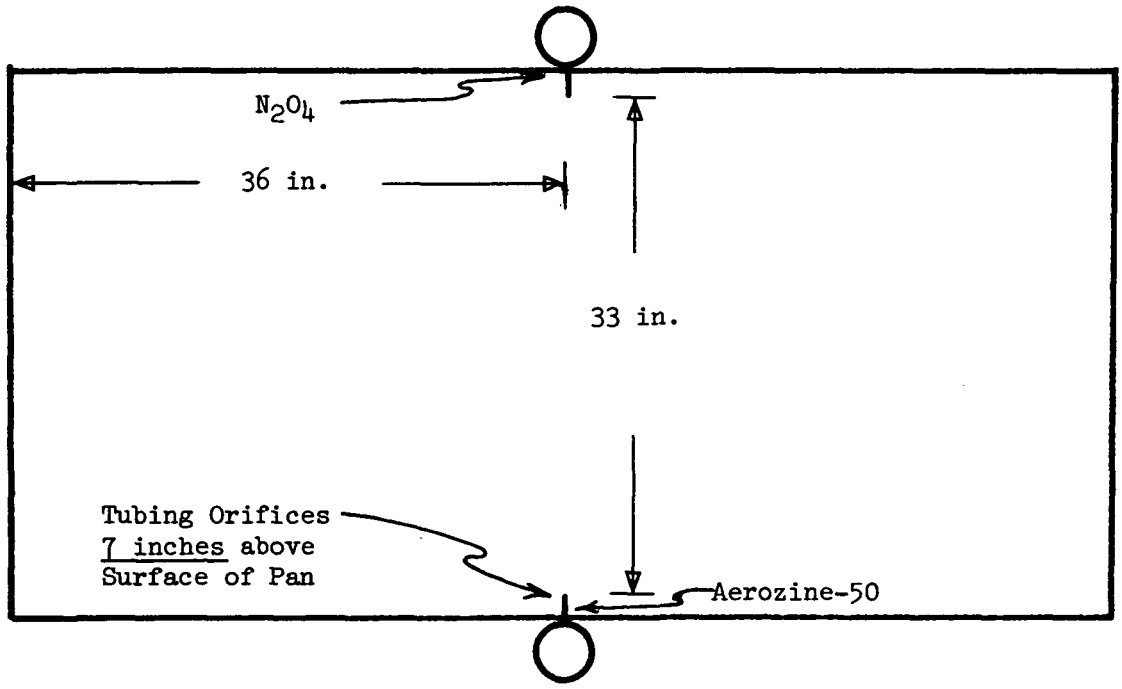


Figure 11: Flowing Spill Through 1/8 Inch Orifices
Tenth Location of Propellant Containers

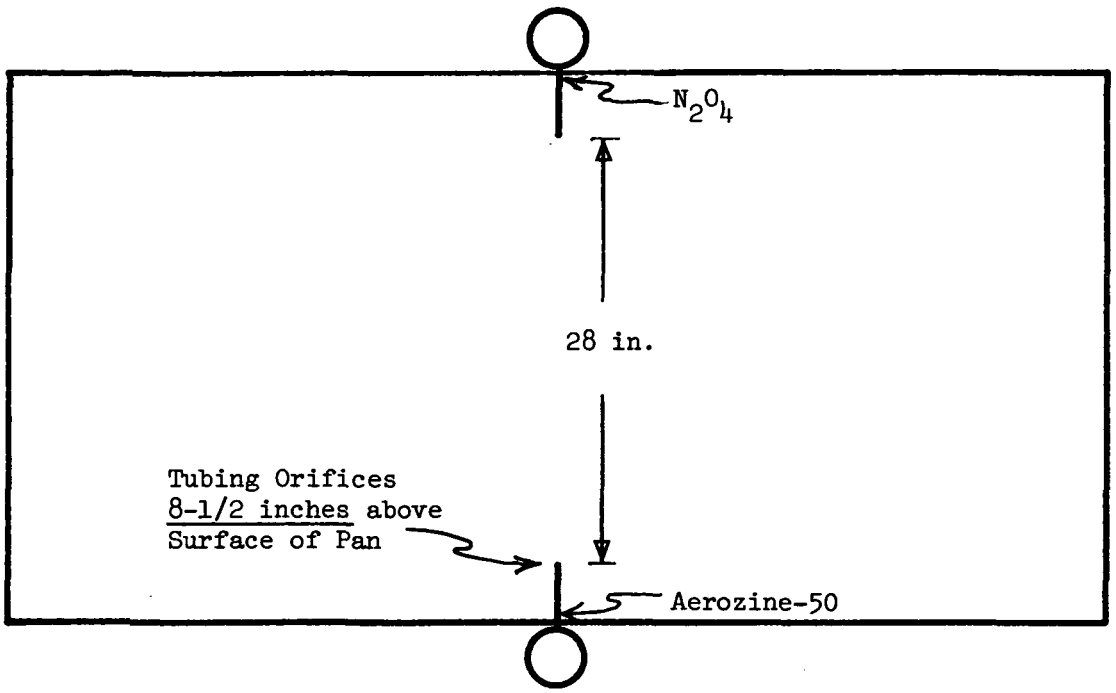


Figure 12: Flowing Spill Through 1/8 Inch Orifices
Eleventh Location of Propellant Containers

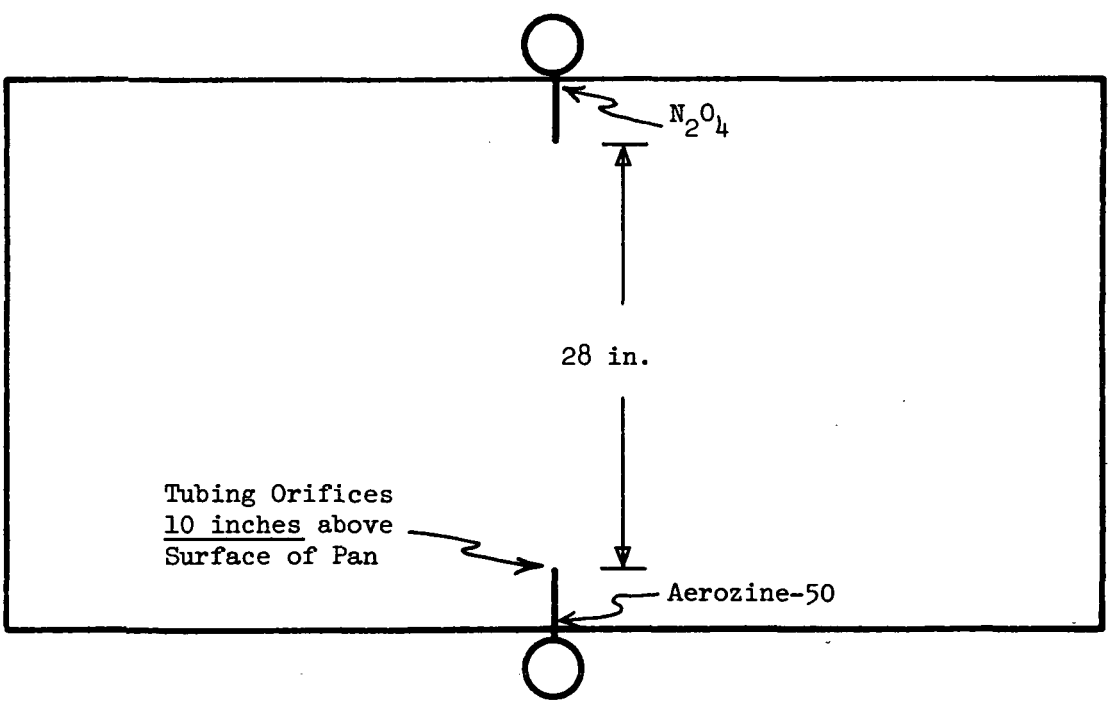


Figure 13: Flowing Spill Through 1/8 Inch Orifices
Twelfth Location of Propellant Containers

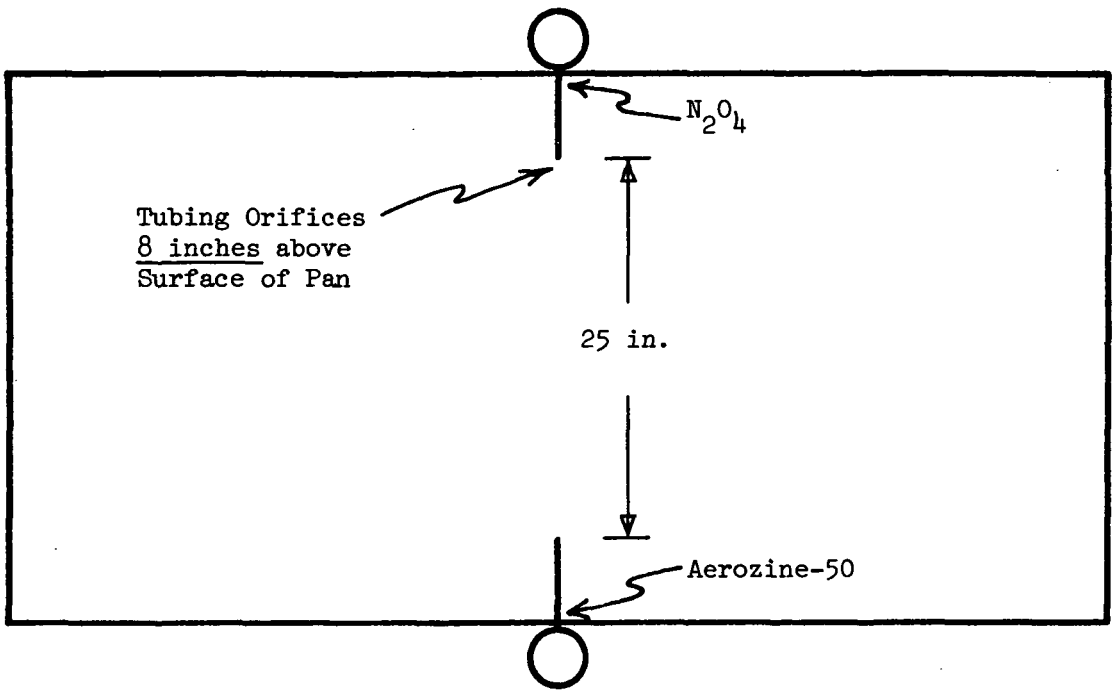


Figure 14: Flowing Spill Through 1/8 Inch Orifices
Thirteenth Location of Propellant Containers

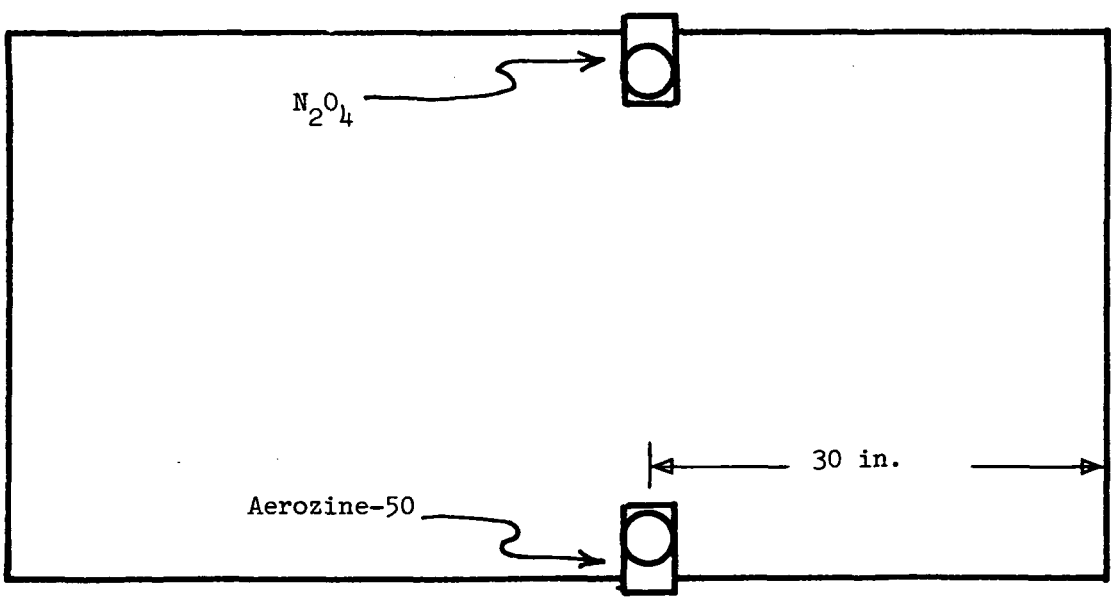


Figure 15: Sudden Sequential Spill
Fourteenth Location of Propellant Containers

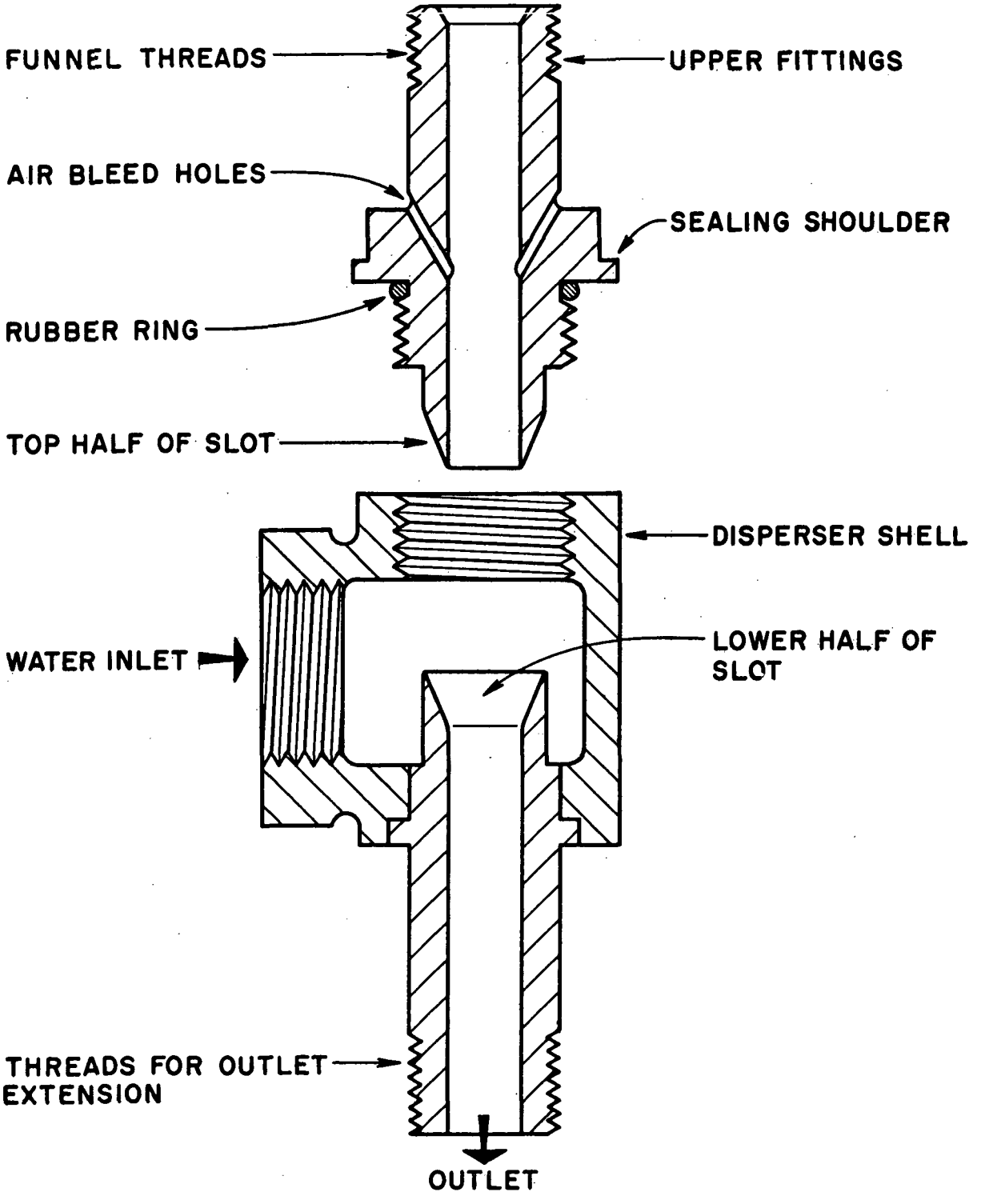


Figure 16: Polymer Disperser Cross-Section

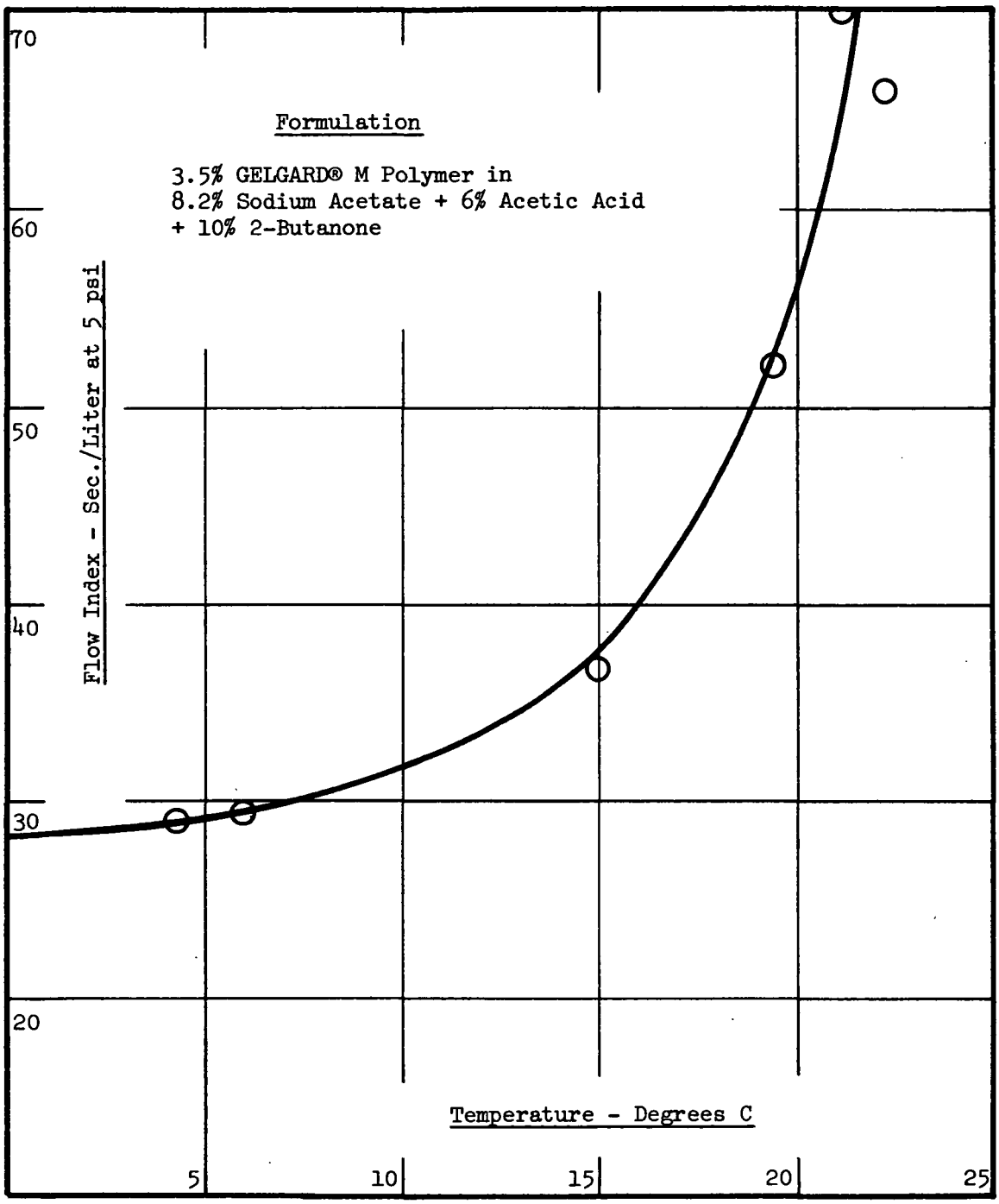


Figure 17: Temperature Dependence of Flow Index

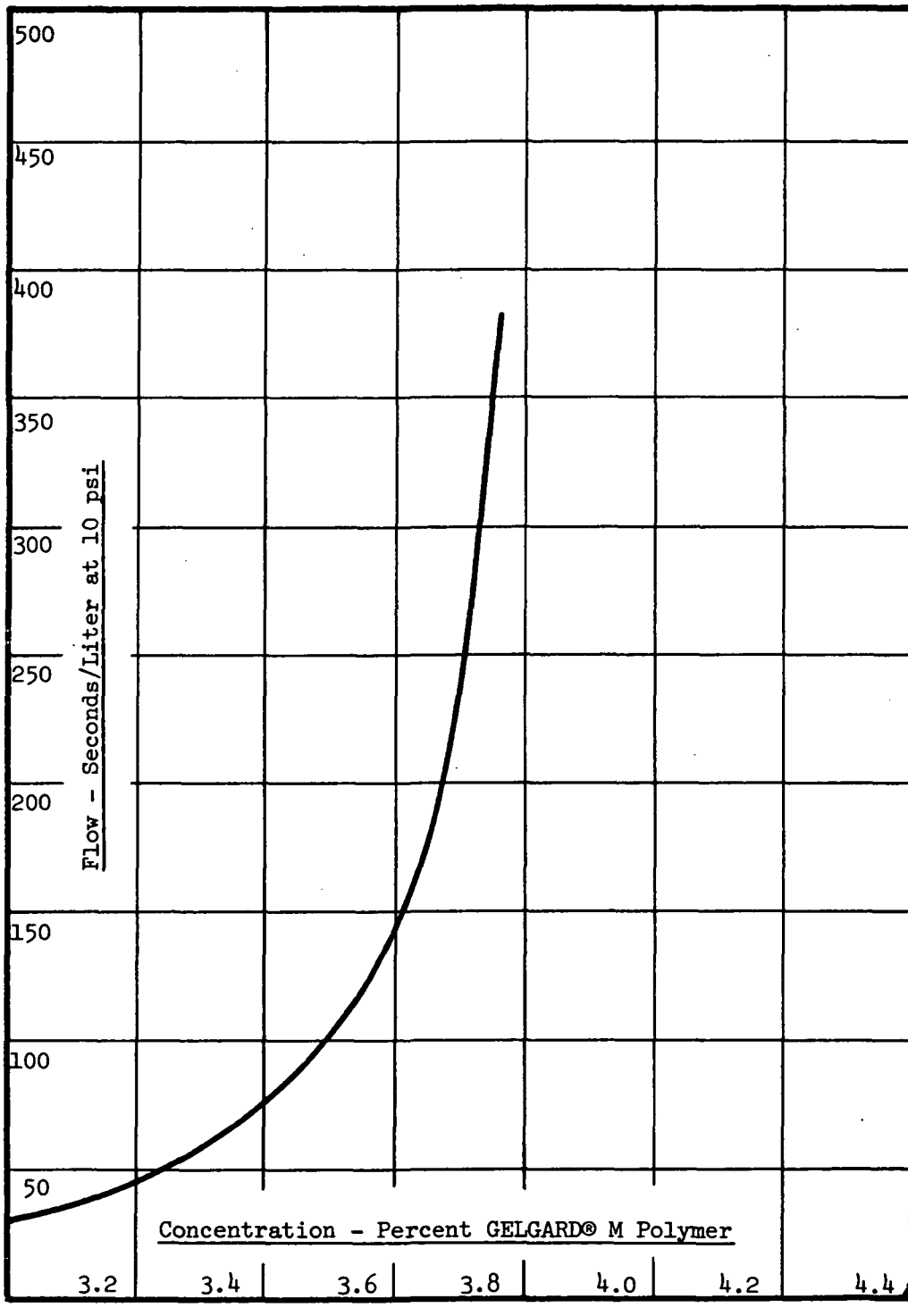


Figure 18: GELGARD® M Polymer Flow Characteristics in 1 Molar Acetic Acid + 1 Molar Sodium Acetate Buffer

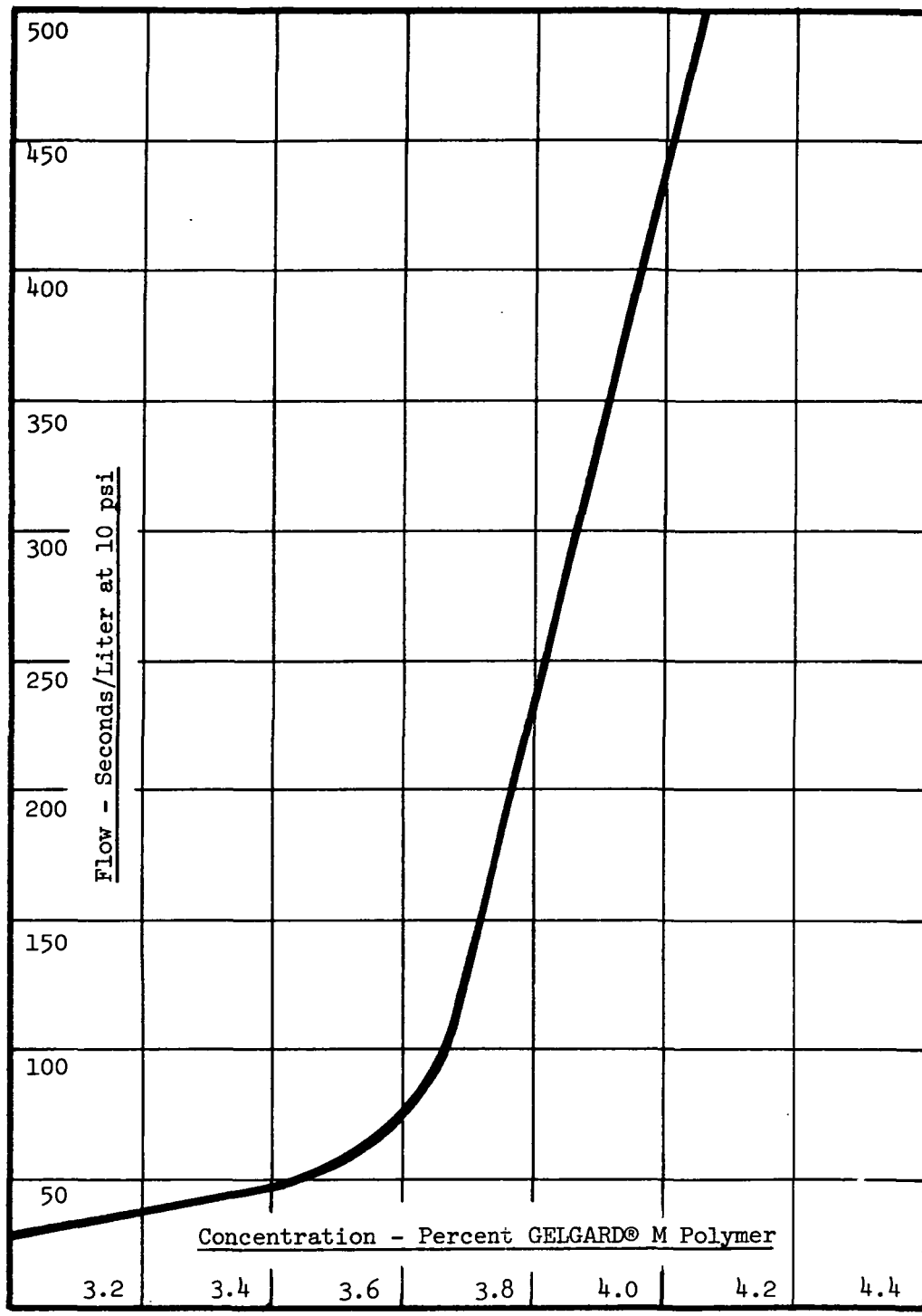


Figure 19: GELGARD® M Polymer Flow Characteristics in a Buffer of 1 Molar Acetic Acid and 1 Molar Sodium Acetate Containing 2 Molar Formaldehyde

APPENDIX C

FILM CATALOGUE

MOVIE HIGHLIGHTS OF THE FIELD TESTING PROGRAM

Reel No.	Scene No.	Film Speed (fps)	Title
1	1	18	Control Series No. 1
1	2	18	Control Series No. 12
1	3	18	Control Series No. 14
1	4	18	Gel Series No. 13
1	5	18	Gel Series No. 14
1	6	24	Gel Series No. 21
1	7	18	Gel Series No. 18
1	8	24	Gel Series No. 19
1	9	24	Gel Series No. 28
1	10	24	Demonstration Series No. 1
1	11	24	Demonstration Series No. 2
1	12	24	Demonstration Series No. 2'
1	13	24	Demonstration Series No. 3
1	14	24	Demonstration Series No. 4
1	15	24	Demonstration Series No. 5
1	16	24	Demonstration Series Reh. Test No. 5

CONTROL SERIES - SCALE UP AND UNCONTROLLED FIRES

Reel No.	Scene No.	Film Speed (fps)	Title
1	1	18	Control Series No. 1
2	1	32	Control Series No. 1
2	2	18	Control Series No. 2
2	3	32	Control Series No. 2
2	4	18	Control Series No. 3*
2	5	32	Control Series No. 3*
2	6	18	Control Series No. 4*
2	7	32	Control Series No. 4*
2	8	18	Control Series No. 5*
2	9	32	Control Series No. 5*
2	10	18	Control Series No. 6*
2	11	18	Control Series No. 9
2	12	18	Control Series No. 10
3	1	18	Control Series No. 11
1	2	18	Control Series No. 12
3	2	18	Control Series No. 13
1	3	18	Control Series No. 14
3	3	18	Control Series No. 15
3	4	18	Control Series No. 16
3	5	18	Control Series No. 17
3	6	18	Control Series No. 18

*Underexposed

WATER CONTROL SERIES

Reel No.	Scene No.	Film Speed (fps)	Title
4	1	18	Water Control Series No. 1
4	2	32	Water Control Series No. 1
4	3	18	Water Control Series No. 2
4	4	18	Water Control Series No. 3
4	5	18	Water Control Series No. 4
4	6	24	Water Control Series No. 5

GELGARD® M POLYACRYLAMIDE SERIES

Reel No.	Scene No.	Film Speed (fps)	Title
5	1	18	Gel Series No. 1
5	2	18	Gel Series No. 2
5	3	18	Gel Series No. 3
5	4	18	Gel Series No. 4
5	5	18	Gel Series No. 4A
5	6	18	Gel Series No. 5
5	7	18	Gel Series No. 6
5	8	18	Gel Series No. 7
5	9	18	Gel Series No. 8
5	10	18	Gel Series No. 9
5	11	18	Gel Series No. 11
6	1	18	Gel Series No. 12
1	4	18	Gel Series No. 13
1	5	18	Gel Series No. 14
6	2	18	Gel Series No. 15
6	3	18	Gel Series No. 16
6	4	18	Gel Series No. 17
1	7	18	Gel Series No. 18
1	8	24	Gel Series No. 19
6	5	32	Gel Series No. 19
6	6	24	Gel Series No. 20
6	7	32	Gel Series No. 20
1	6	24	Gel Series No. 21
6	8	24	Gel Series No. 23
7	1	24	Gel Series No. 24
7	2	24	Gel Series No. 25
7	3	24	Gel Series No. 27
1	9	24	Gel Series No. 28
7	5	24	Gel Series No. 29

DEMONSTRATION SERIES

Reel No.	Scene No.	Film Speed (fps)	Title
8	1	24	Demonstration Series No. 1'
1	12	24	Demonstration Series No. 2'
8	2	24	Demonstration Series No. 5'
8	3	24	Demonstration Series No. 5A
8	4	24	Demonstration Series No. 5B
8	5	24	Demonstration Series No. 2A
8	6	24	Demonstration Series No. 5C
8	7	24	Demonstration Series No. 1A
8	8	24	Demonstration Series No. 2C
9	1	24	Demonstration Series No. 3A
9	2	24	Demonstration Series No. 4A
9	3	24	Demonstration Series No. 5D
9	4	24	Demonstration Series No. 6
9	5	24	Demonstration Series No. 7
9	6	24	Demonstration Series Reh. Test No. 1
9	7	24	Demonstration Series Reh. Test No. 2
9	8	24	Demonstration Series Reh. Test No. 3
9	9	24	Demonstration Series Reh. Test No. 4
1	16	24	Demonstration Series Reh. Test No. 5
10	1	24	Demonstration Series No. 1*
10	2	24	Demonstration Series No. 2*
10	3	24	Demonstration Series No. 3*
10	4	24	Demonstration Series No. 4*
10	5	24	Demonstration Series No. 5*

*These close-up views were taken by an Ames Research Center photographer.

APPENDIX D

Safety Procedures for Hypergolic Fire Experiments

I. PROPELLANTS

A. The oxidizer is N_2O_4 delivered in 120 pound cylinders and will be used in quantities up to one quart. Small releases will be made first and their effect monitored at the Dow property line.

B. The fuel is a mixture of 50% hydrazine and 50% UDMH. It will be obtained in I.C.C. approved 5-gallon containers and mixed just prior to use. The containers will be maintained under a nitrogen blanket of 25-30 inches of H_2O pressure which is adequate pressure to expell the fuel from the storage container when it is withdrawn for use. They will also be provided with an approved eductor pipe for withdrawing the fluid.

C. Both the oxidizer cylinder and the fuel containers will be properly grounded and will be stored in open sheds. The sheds must permit adequate ventilation as well as protection from the direct hot rays of the sun. The sheds will be provided with a removable front wall to prevent vandalism.

D. The fuel and the oxidizer will be stored in separate sheds located approximately 50 feet apart. They will be located crosswind from the prevailing wind direction.

E. Plastic trays will be placed below all filling spouts to prevent any spillage from entering the ground.

F. All electrical equipment within 25 feet of the storage areas will be explosion proof.

G. All tools used around the fuel storage tanks will be spark-proof tools.

H. The nitrogen used for the nitrogen pad on the fuel can be either oil pumped or water pumped nitrogen.

I. The nitrogen pad system will include an 8 foot water leg and vent line or a low pressure regulator and pop-off valve to permit the storage tank to breath. This is especially necessary because of the wide temperature swing between daytime and nighttime.

II. PERSONNEL AND SAFETY EQUIPMENT

A. Only properly trained and qualified personnel will participate in the procedures. Cars will be parked off of the road and outside the second rope area

B. Dave Bauer or Dick Oblander (ext. 288) must be notified the day before any tests so that he can notify the Bay Area Air Quality Board. Any infractions could cause a shutdown of the project.

C. The secretary of the plant fire department (phone ext. 210) will be notified before any test operations are started. She will notify the garage foreman who will advise all truck drivers to stay out of the East Field.

D. The rope barrier will be placed across the road before any test begins and a quick visual inspection of the downwind area will be made immediately preceding each spill.

E. During actual burning operations only people necessary to the operation will be permitted within the internal work area bounded by rope and signs. Safety glasses and hard hats will be worn at all times (except when wearing an Acid King Suite).

F. Full face gas masks or cannister respirators with just a mouthpiece will be worn by all persons within the internal work area. When using a mouthpiece instead of a gas mask, goggles will be worn to protect the eyes from the fumes. These will only be needed if there is an unexpected change in the wind direction during the actual test.

G. Observers without respiratory apparatus must remain outside of the secondary area which is also bounded by ropes.

H. During actual burning operations, two men will always be suited up in Acid King sealed suits containing hard hats. The suits will be attached to fresh air breathing tanks supplied by the plant fire department.

I. These men will wear vinyl-coated or neoprene over gloves.

J. Before each burning, a smoke bomb will be burned to confirm that the wind direction is such that the plume will remain within the acceptable area as outlined by permanent markers placed 200 feet downwind from the burn pan.

K. The cameraman will always have a Freon type of portable air horn available for obtaining the attention of the men in the Acid King Suits in case of an emergency.

L. In case of a plant emergency, the plant protection department will advise us by phone and no fires are to be started until

the "all-clear" signal. Personnel are not to try to evacuate the area. They are to remain in the area and have self-contained breathing equipment in readiness in case the emergency is a gas leak.

III. PROCEDURE FOR APPLYING NITROGEN BLANKET TO THE HYDRAZINE AND UDMH STORAGE TANKS

A. The I.C.C. shipping drum will be placed upright inside the tray. The tray will be filled with water and shaved ice to keep the fuel as cool as practical.

B. Grounding wires will be attached to the tray and also to the drum. They will be attached to a well-grounded rod.

C. While wearing full-protective clothing and breathing apparatus, cautiously and slowly loosen the 2" bung using explosion-proof tools. After the internal pressure is released, remove the plug.

D. Replace the plug with a clean eductor pipe using a Teflon or polyethylene gasket. The eductor pipe will terminate with a stainless steel valve. Be sure it is closed before applying any nitrogen pressure. The nitrogen supply line will be disconnected during this operation.

E. After turning the regulator to zero output by unscrewing the adjustment handle, open the nitrogen cylinder valve

wide. Then adjust the regulator to provide a small nitrogen flow to purge the line. Not more than 3-4 psi on the regulator at zero flow. THEN connect the N_2 supply line to the nitrogen tap on the eductor pipe.

F. Place drip pot under the eductor pipe outlet.

G. Open the valve at the end of the eductor pipe. When fluid begins to flow into drip pot, the eductor tube has been properly filled and the valve can be closed.

H. Observe the regulator to be sure pressure does not exceed 4 psig.

I. Rinse the drip pot with water and replace it half filled with water.

IV. PROCEDURE FOR FILLING THE REACTANT POTS ON THE FIRE PAN AND STARTING THE FIRE

A. The fuel and oxidizer pots are permanently marked to prevent interchanging them.

B. Because of the hot weather, the pots will be kept in polyethylene coolers or ice baths before use so there is less gassing off during these pre-fire operations. A separate cooler will be used for the two different pots. The same man will always handle the same component.

C. During the time that either operator is loading the pot with either fuel or oxidizer, the second operator will remain in the waiting area and act as a safety backup man. A pressurized hose and spray nozzle will always be available to him at this waiting area.

D. The fuel will always be filled first. Remove the clean pot from the cooler and carry it to the fuel storage area. Wipe out any condensate and place it on the table. Use a polyethylene graduate for measuring the liquid volume of hydrazine required. Pour it into the metal pot. Repeat with UDMH using the same polyethylene graduate. Stir with a non-sparking spatula for 15 seconds. The metal pot is to remain on the table during all of these operations so there is no chance of dropping it or spilling it.

E. Place the cover on the pot and carry the mixture to the fire pan and lock it into its recess on the tilt mechanism. The cover is to contain the fumes as much as possible.

F. After this is completed, the first operator will go to the waiting area and the second man suited up will then take the oxidizer pot from the ice bath and set it on the table. Wipe out any condensate present. Draw the required amount of oxidizer into a polyethylene graduate. Pour it into the metal pot which is sitting on the table.

G. Cover the oxidizer pot and lock it into its recess on the tilt mechanism of the fire pan.

H. Both men suited up will then move to the waiting area and wait for a signal from the cameraman.

I. After the cameras are started, the cameraman will signal the men and the tilt mechanism will be tripped.

J. The cameras will continue to roll and the nozzle man will proceed forward and apply the extinguishing material to the fire. This operation will automatically start the timer.

K. The second man suited up will remain in the waiting area with the water hose for any emergency.

L. After the fire is completely extinguished, the fire pan will be rinsed and dried in preparation for another test. The fuel pots will be washed and placed in the proper ice bath.

M. The temperature of the water in the water bath will be recorded both before and after each run. The temperature will be adjusted if necessary.

N. The men suited up will not remove their helmets until they are inside the change building because they will be without eye and head protection. Before leaving the change room, they will don safety glasses and hard hats.

V. PROCEDURE FOR STORING AND HANDLING THE OXIDIZER

A. The oxidizer (N_2O_4) will be purchased in 120 pound cylinders from the Matheson Company.

B. It will be stored in an open shed but protected from the direct rays of the sun. The shed will be located crosswind from the shed used for the fuel storage.

C. The cylinder will be placed in a tray and securely chained to the shed.

D. The recommended S.S. throttle valve will be used.

E. Due to the excessive heat that can be encountered during the hot summer, the cylinder will be wrapped with fiber glass matting or plastic cloth and a continuous small stream of water will be used to keep it moist. This will give uniform temperature control to yield more reproducible date.

VI. INITIAL CHECK-OUT LIST PRECEDING FIRST BURN

A. Be sure extension 288 has notified Air Quality Board of test schedule.

B. Test eyebath, shower, emergency hose pressure. Place Freon air horn on camera stand.

C. Notify Plant Protection secretary - ext. 210. Put rope and barrier across the road.

D. Drain water and inhibitor from the fire pan. Squeegee.

E. Fill all gasoline engines with fuel and oil.

F. Adjust temperature of water in the fire pan.

G. Pressurize Pfaudler Tank -- do not operate with less than 200 psi in 6 pack nitrogen unit.

H. Adjust coolant flow to Pfandler jacket.

I. Set clock to correct time.

J. Start up both fans.

VII. CHECK-OUT LIST PRECEDING EACH TEST

A. Fill in all data on Data Sheet.

B. Be sure timer clock is reset to zero.

C. Inspect downwind area for intruders. Advise all observers to go beyond second rope barrier.

D. Don Acid King Suits.

E. Open valve on GELGARD® nozzle and eject enough GELGARD to fill the hose with cool solution. Measure and record its temperature.

F. Load fuel and oxidizer.

VIII. SHUTDOWN AND DECONTAMINATION PROCEDURE AT END OF EACH DAY

A. Clean fire pan and fill with water plus 200 ppm sodium sulfite inhibitor.

B. Suited operators to shower and remove suits.

C. Stow all equipment.

D. Record quantity of fuel and oxidizer consumed that day on the clip board.

E. Blow down the Pfaudler kettle pressure.

F. Adjust N_2 pad pressure on fuel tanks to about 3 psig. Lock the shed.

G. Shut off main cylinder valve on the N_2O_4 cylinder. Lock the shed.

H. Shut off main water supply valve on hydrant.

I. Notify plant protection, ext. 210, that the area is shut down and they can replace the breathing air trailers.

J. Remove rope and barrier from the road.

7-29-71

HYDRAZINE (Anhydrous) H_2NNH_2

DESCRIPTION: Clear liquid with an ammonia-like odor.

FIRE AND EXPLOSION HAZARDS: Flammable liquid. Highly reactive reducing agent. Vapor forms explosive mixtures with air over a wide range. Flammable limits, 4.7% and 100%. Flash point, 100° F. Ignition temperature varies, 75° F. (iron rust surface) and 518° F. (glass surface). Vapor-air density at 100° F., 1.0. Hydrazine may ignite spontaneously in air when in contact with porous materials such as earth, asbestos, wood or cloth. Spontaneous ignition can occur with oxidants like hydrogen peroxide and nitric acid. Contact with many metallic oxide surfaces may lead to flaming decomposition. Soluble in water.

LIFE HAZARD: Vapors are very toxic and attack eyes and respiratory system. Liquid is corrosive to skin. In case of contact, wash immed ate y with water. Wear full protective clothing.

FIRE FIGHTING PHASES: Flood with water. Dry chemical and carbon dioxide may be used to extinguish the fire, but flooding with water will be necessary to prevent reignition. "Alcohol" foam is effective on spill fires. In advanced or massive fires, fire fighting should be done from a safe distance or from a protected location. Use water to keep fire-exposed containers cool. If a leak or spill has not ignited, use water spray to disperse the vapors. If it is necessary to stop a leak, use water spray to protect men attempting to do so. Water spray may be used to flush spills away from exposures and to dilute spills to nonflammable mixtures. Wear full protective clothing.

USUAL SHIPPING CONTAINERS: Glass bottles and carboys in wooden boxes; stainless steel cans, drums, tanks, and tank trucks.

STORAGE: Protect against physical damage. Outside or detached storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Separate from oxidizing materials such as metal oxides, peroxides, and acids. Provide water for flushing spills or leaks. Tanks should be located in water-filled dikes. Protect against electrical sparks, open flames, or any heat source. A nitrogen atmosphere should be maintained over anhydrous hydrazine.

REMARKS: Electrical installations in Class I hazardous locations, as defined in Article 500 of the National Electrical Code, should be in accordance with Article 501 of the Code; and electrical equipment should be suitable for use in atmospheres containing hydrazine vapors. See Flammable and Combustible Liquids Code (NFPA No. 30), National Electrical Code (NFPA No. 70), Static Electricity (NFPA No. 77), and Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids (NFPA No. 325M).

UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH) $(CH_3)_2NNH_2$

DESCRIPTION: Colorless liquid with a sharp, ammonia-like odor.

FIRE AND EXPLOSION HAZARDS: Flammable liquid. Vapor forms flammable mixtures with air over a wide range. Flammable limits, 2% and 95%. Flash point, about 5° F. Ignition temperature, 480° F. Vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. Spontaneous ignition can occur on contact with oxidants like fuming nitric acid and hydrogen peroxide. Soluble in water.

LIFE HAZARD: The vapor is very toxic and attacks eyes and respiratory system. Liquid is corrosive to the skin. Wear full protective clothing.

FIRE FIGHTING PHASES: Flood with water. Small fires can be extinguished with carbon dioxide and dry chemical. Wear full protective clothing.

USUAL SHIPPING CONTAINERS: Glass bottles and carboys in wooden boxes, mild or stainless steel cans, drums, tanks.

STORAGE: Protect against physical damage. Outside or detached storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Storage temperature should be less than 120°F. Separate from oxidants like nitric acid, hydrogen peroxide, and halogens, and check periodically for decomposition. Provide water for flushing spills or leaks. A nitrogen atmosphere should be maintained over anhydrous UDMH.

REMARKS: Where explosionproof electrical equipment is required by the National Electrical Code, it shall be Class I, Group C equipment. See Flammable and Combustible Liquids Code (NFPA No. 30), National Electrical Code (NFPA No. 70), Static Electricity (NFPA No. 77), and Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids (NFPA No. 325M).

NITROGEN TETROXIDE N_2O_4

DESCRIPTION: Yellowish-brown gas which is easily liquefied to a dense brown corrosive liquid. Boiling point, 70° F. Normally it is handled as a liquid. Nitrogen tetroxide is in equilibrium with nitrogen dioxide.

FIRE AND EXPLOSION HAZARDS: Nitrogen tetroxide, itself, will not burn. However, it is an extremely strong oxidizing agent and may cause fire on contact with clothing and other combustible materials. The reactions between nitrogen tetroxide and both ordinary fuels and rocket fuels and between nitrogen tetroxide and most chlorinated hydrocarbons, may be violent.

LIFE HAZARD: Vapors are extremely toxic and may cause fatal lung damage even in very dilute concentrations. Both the liquid and vapor may cause severe eye and skin burns. Wear full protective clothing. Anyone exposed even momentarily to high concentrations should receive immediate medical attention.

FIRE FIGHTING PHASES: Use water to keep fire-exposed containers cool. If it is necessary to stop the flow of gas, use water spray to direct escaping gas away from men effecting the shut-off. Wear full protective clothing.

USUAL SHIPPING CONTAINERS: 125-pound and 150-pound steel cylinders, 1-ton containers and 50-ton tank cars.

STORAGE: Protect containers against physical damage. Separate from combustible, organic or other readily oxidizable materials. Transfer facilities should be located out of doors. Because nitrogen tetroxide is extremely corrosive when wet, proper materials of construction are necessary.

BIOCHEMICAL RESEARCH DEPARTMENT

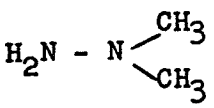
THE DOW CHEMICAL COMPANY

MIDLAND MICHIGAN

DATA SHEET OF PROPERTIES, HEALTH HAZARDS, AND PRECAUTIONS FOR SAFE HANDLING OF MATERIALS

MOLECULAR FORMULA	CHEMICAL NAME
$C_2H_8N_2$	a sym. Dimethyl Hydrazine
MOLECULAR WEIGHT / **INDUSTRIAL HYGIENE STANDARD**	**SYNONYMS**
60.1 / 0.5 ppm (T)	

STRUCTURAL FORMULA - OR COMPOSITION



PHYSICAL AND CHEMICAL PROPERTIES

BOILING POINT	EXPLOSIVE LIMITS (% BY VOL. IN AIR)	FLASH POINT	IGNITION TEMP.	MELTING POINT	VAPOR PRESSURE mm Hg 25°C
63.3 °c 760mmHg.		34 °C. °F.	°c.	-58 °c.	157

CORROSIVENESS (To Common Metals)	PHYSICAL STATE	COLOR
	Liquid	Colorless

CHEMICAL REACTIVITY	ODOR (Include Concentration in Air)
Can react vigorously with oxidizing materials.	Ammoniacal, fishy - threshold 6-14 ppm

STABILITY (To pH Change, Heat, Light)

TOXIC PROPERTIES

TYPE OF CONTACT		CLASSIFICATION OF TOXIC PROPERTIES	
EYE		☐ May cause no response or no more than very slight to slight transitory pain and/or irritation of the eyelids.	☒ May cause some permanent loss of vision (this includes damage to cornea or internal injury which is incompletely healed in one week.)
		☐ May cause sufficient injury to the eye to result in loss of time from work. (This includes damage to the cornea which heals or nearly heals in a week and/or considerable conjunctival irritation with edema.)	☐ Vapor exposure may cause severe pain, lacrymation or serious injury to the eyes.
SKIN		☐ Single prolonged exposure (hours) causes no effect. Several repeated prolonged exposures may or may not cause the development of some slight irritation.	☐ Single short exposure (minutes) may cause considerable irritation and/or single prolonged or frequently repeated short exposures cause a burn and/or may cause systemic injury, even death.
		☐ Single prolonged exposure may cause some reddening of the skin. Repeated prolonged contacts may cause appreciable irritation, possibly a mild burn and/or may cause appreciable systemic injury due to absorption.	☒ An exposure rapidly causes severe burns and/or serious systemic injury, even death.
INHALATION	DUST OR MIST	☐ No systemic injury expected. No irritation to nose and throat in dusty or misty atmospheres.	☐ Dusty or misty atmosphere painful to nose and throat (intolerable to most people) and/or exposure may cause serious systemic injury.
		☐ Throat and nose irritation in a dusty or misty atmosphere is painful but not intolerable and/or prolonged or repeated exposures may cause systemic injury.	☐ Short exposure (minutes) may cause death or serious systemic injury.
	VAPOR	☐ Exposures do not cause any effects other than some very slight irritation or pain to the eyes or respiratory passages at the most.	☐ Exposures may cause extreme drowsiness, and/or serious systemic injury, and/or may cause intolerable irritation to the respiratory passages.
		☐ Single exposures exceeding 1/2 hour, or frequently repeated exposures of shorter duration, may cause slight anesthesia and/or slight systemic injury, and/or cause appreciable, but not intolerable, irritation of respiratory passages.	☐ Short exposures may cause unconsciousness, and/or serious systemic injury, including death.
		☒ Even very short exposure will cause serious systemic injury or death.	
INGESTION		☒ Amounts which may be swallowed incidental to industrial handling will not cause injury. However, if substantial quantities should be swallowed, more or less serious effects may occur.	☐ Amounts which may be swallowed incidental to industrial handling and use may cause serious injury.

COMMENTS

DEGREES OF EXPOSURE RELATED TO TYPES OF OPERATION			PRECAUTIONS (SEE CODE BELOW)				
			EYES	SKIN	INHALATION*		INGESTION
					DUST OR MIST	VAPOR	
I	NO CONTACT	Characterized by remote operation with equipment isolated from the work area. The persons entering isolated areas will require the personal protection outlined for IV below.	A	A		A	A
II	MINOR CONTACT	Characterized by closed systems with equipment vented outside the work area; instrument control; mechanical handling of materials in bulk. Examples are: continuous reactors, stills and filters; enclosed conveyors; ventilated packaging.	C	D		A*	A
III	OCCASIONAL DAILY CONTACTS	Characterized by manual handling of materials in packages such as bags, drums and fiberpaks. Ventilation may be provided for specific jobs. Many batch operations fall into this category.	D	E		D	A
IV	GROSS CONTACT LIKELY	Characterized by hand operation. Examples are: Emergency repairs, cleaning equipment, cleaning filters, taking care of spills, packaging volatile or dusty materials without ventilation, wheeling and tray drying.	D	E		E**	A

EYE CONTACT

- A No eye protection needed.
- B Use safety glasses without side shields.
- C Use safety glasses with side shields.
- D Use chemical workers goggles.
- E Use gas tight goggles or a full face gas mask.

SKIN CONTACT**

- A A bath and clean clothes once per week along with the usual washing at mealtimes should be adequate precautions.
- B Grossly contaminated clothing and shoes must be removed not later than the end of the work period and must be thoroughly cleaned before re-use.
- C Require shower at the end of the work period and clean clothing from the skin out at the start of each work day.
- D Clothing should be changed and skin washed promptly upon any detectable contact. Each use will require special consideration to determine suitable protective devices and standards of personal cleanliness.
- E Impervious clothing such as rubber boots, rubber aprons, and rubber gloves will be required. Specific items will be dictated as required by circumstance.

INHALATION

DUST OR MIST

- A No respiratory protection.
- B No protection required for exposure of thirty min. duration or less to obviously dusty atmospheres. Exposures of longer duration will require the use of a dust respirator bearing the approval of the U. S. Bureau of Mines for the use with toxic dusts.
- D Any exposure to obviously dusty atmospheres will require a dust respirator bearing the approval of the U. S. Bureau of Mines for use with toxic dusts.
- E Any exposure to dusty atmospheres will require the use of an airline respirator, blower mask, or Chemox mask.

VAPOR

- A No precautions necessary.
- B No precautions necessary for single exposures of less than 1/2 hour. Longer single exposures, or frequently repeated exposures will require a gas mask or respirator equipped with appropriate canister.
- C No precautions necessary for single exposures of no more than ten minutes. Longer exposures either single or repeated, will require gas mask or respirator equipped with appropriate canister.
- D Gas mask with appropriate canister required at all times.
- E Evacuate area at once and enter only with airline respirator, blower mask or Chemox mask.

INGESTION

- A No unusual procedures required.
- E Food and tobacco should not be present in the work area. Hands and face should be washed before smoking and eating.

COMMENTS

**GOOD PRACTICE REQUIRES THAT GROSS AMOUNTS OF ANY CHEMICAL BE REMOVED FROM THE SKIN AS SOON AS IS PRACTICAL

** If air concentrations are high, caution should be exercised in entering the area even with respiratory protection as skin irritation may result.

* The "A" applies provided only that air concentrations are monitored continuously, otherwise "D" applies.

*SUITABLE GAS MASK CANISTER

Organic vapor canister may offer suitable protection, but no tests have been made to prove that contention.

SIGNED J. E. Peterson CHECKED D. D. McCollister

DATE 3-16-59 DATE 3-20-59

1219-156 PRINTED IN U.S.A. 58-87

BIOCHEMICAL RESEARCH DEPARTMENT

THE DOW CHEMICAL COMPANY

MIDLAND MICHIGAN

DATA SHEET OF PROPERTIES, HEALTH HAZARDS, AND PRECAUTIONS FOR SAFE HANDLING OF MATERIALS

MOLECULAR FORMULA	CHEMICAL NAME
H_4N_2	Hydrazine
MOLECULAR WEIGHT	**INDUSTRIAL HYGIENE STANDARD**	**SYNONYMS**
32.05	1 ppm, 1.3 mg/m^3	

STRUCTURAL FORMULA - OR COMPOSITION

H_2N-NH_2

PHYSICAL AND CHEMICAL PROPERTIES

BOILING POINT	EXPLOSIVE LIMITS (% BY VOL. IN AIR)	FLASH POINT	IGNITION TEMP.	MELTING POINT	VAPOR PRESSURE mm Hg 25°C
113.5 °c 762 mmHg.	4.7-100	126 °F.	270 °c.	0 °c.	10.4 mm (20°C)

CORROSIVENESS (To Common Metals)	PHYSICAL STATE	COLOR
Reacts with iron oxides, Mo oxides, "316" stainless steel.	Liquid	Brown or colorless

CHEMICAL REACTIVITY	ODOR (Include Concentration in Air)
Powerful reducing agent	Ammoniacal, fishy or amine-like 3-4 ppm

STABILITY (To pH Change, Heat, Light)

Explodes during distillation if traces of air are present.

TOXIC PROPERTIES

TYPE OF CONTACT		CLASSIFICATION OF TOXIC PROPERTIES	
EYE		☐ May cause no response or no more than very slight to slight transitory pain and/or slight transient corneal injury and/or irritation of the eyelids.	☒ May cause some permanent loss of vision (this includes damage to cornea or internal injury which is incompletely healed in one week.)
		☐ May cause sufficient injury to the eye to result in loss of time from work. (This includes damage to the cornea which heals or nearly heals in a week and/or considerable conjunctival irritation with edema.)	☒ Vapor exposure may cause severe pain, lacrymation or serious injury to the eyes.
SKIN		☐ Single prolonged exposure (hours) causes no effect. Several repeated prolonged exposures may or may not cause the development of some slight irritation.	☐ Single short exposure (minutes) may cause considerable irritation and/or single prolonged or frequently repeated short exposures cause a burn and/or may cause systemic injury, even death.
		☐ Single prolonged exposure may cause some reddening of the skin. Repeated prolonged contacts may cause appreciable irritation, possibly a mild burn and/or may cause appreciable systemic injury due to absorption.	☒ An exposure rapidly causes severe burns and/or serious systemic injury, even death.
INHALATION	DUST OR MIST	☐ No systemic injury expected. No irritation to nose and throat in dusty or misty atmospheres.	☐ Dusty or misty atmosphere painful to nose and throat (intolerable to most people) and/or exposure may cause serious systemic injury.
		☐ Throat and nose irritation in a dusty or misty atmosphere is painful but not intolerable and/or prolonged or repeated exposures may cause systemic injury.	☐ Short exposure (minutes) may cause death or serious systemic injury.
	VAPOR	☐ Exposures do not cause any effects other than some very slight irritation or pain to the eyes or respiratory passages at the most.	☐ Exposures may cause extreme drowsiness, and/or serious systemic injury, and/or may cause intolerable irritation to the respiratory passages.
		☐ Single exposures exceeding 1/2 hour, or frequently repeated exposures of shorter duration, may cause slight anesthesia and/or slight systemic injury, and/or cause appreciable, but not intolerable, irritation of respiratory passages.	☒ Short exposures may cause unconciousness, and/or serious systemic injury, including death.
		☐ Even very short exposure will cause serious systemic injury or death.	
INGESTION		☐ Amounts which may be swallowed incidental to industrial handling will not cause injury. However, if substantial quantities should be swallowed, more or less serious effects may occur.	☒ Amounts which may be swallowed incidental to industrial handling and use may cause serious injury.

COMMENTS

Hydrazine

	DEGREES OF EXPOSURE RELATED TO TYPES OF OPERATION		PRECAUTIONS (SEE CODE BELOW)				
			EYES	SKIN	INHALATION*		INGESTION
					DUST OR MIST	VAPOR	
I	NO CONTACT	Characterized by remote operation with equipment isolated from the work area. The persons entering isolated areas will require the personal protection outlined for IV below.	A	A		A	A
II	MINOR CONTACT	Characterized by closed systems with equipment vented outside the work area; instrument control; mechanical handling of materials in bulk. Examples are: continuous reactors, stills and filters; enclosed conveyors; ventilated packaging.	C	A		A*	A
III	OCCASIONAL DAILY CONTACTS	Characterized by manual handling of materials in packages such as bags, drums and fiberpaks. *Ventilation may be provided for specific jobs. Many batch operations fall into this category.*	E	D		D	E
IV	GROSS CONTACT LIKELY	Characterized by hand operation. Examples are: Emergency repairs, cleaning equipment, cleaning filters, taking care of spills, packaging volatile or dusty materials without ventilation, wheeling and tray drying.	E	E		E	E

EYE CONTACT

- A No eye protection needed.
- B Use safety glasses without side shields.
- C Use safety glasses with side shields.
- D Use chemical workers goggles.
- E Use gas tight goggles or a full face gas mask.

SKIN CONTACT**

- A A bath and clean clothes once per week along with the usual washing at mealtimes should be adequate precautions.
- B Grossly contaminated clothing and shoes must be removed not later than the end of the work period and must be thoroughly cleaned before re-use.
- C Require shower at the end of the work period and clean clothing from the skin out at the start of each work day.
- D Clothing should be changed and skin washed promptly upon any detectable contact. Each use will require special consideration to determine suitable protective devices and standards of personal cleanliness.
- E Impervious clothing such as rubber boots, rubber aprons, and rubber gloves will be required. Specific items will be dictated as required by circumstance.

INHALATION

DUST OR MIST

- A No respiratory protection.
- B No protection required for exposure of thirty min. duration or less to obviously dusty atmospheres. *Exposures of longer duration will require* the use of a dust respirator bearing the approval of the U. S. Bureau of Mines for the use with toxic dusts.
- D Any exposure to obviously dusty atmospheres will require a dust respirator bearing the approval of the U. S. Bureau of Mines for use with toxic dusts.
- E *Any exposure to dusty atmospheres will require the use of an airline* respirator, blower mask, or Chemox mask.

VAPOR

- A No precautions necessary.
- B No precautions necessary for single exposures of less than 1/2 hour. Longer single exposures, or frequently repeated exposures will require a gas mask or respirator equipped with appropriate canister.
- C No precautions necessary for single exposures of no more than ten minutes. Longer exposures either single or repeated, will require gas mask or respirator equipped with appropriate canister.
- D Gas mask with appropriate canister required at all times.
- E Evacuate area at once and enter only with airline respirator, blower mask or Chemox mask.

INGESTION

- A No unusual procedures required.
- E Food and tobacco should not be present in the work area. Hands and face should be washed before smoking and eating.

COMMENTS

**GOOD PRACTICE REQUIRES THAT GROSS AMOUNTS OF ANY CHEMICAL BE REMOVED FROM THE SKIN AS SOON AS IS PRACTICAL

*SUITABLE GAS MASK CANISTER

Organic Vapor

* Adequate control of vapors must be shown by air analysis.

SIGNED Carl L. Hake CHECKED H. R. Hoyle

DATE 2/2/62 REVISED DATE 2/2/62 REVISED

BIOCHEMICAL RESEARCH DEPARTMENT

THE DOW CHEMICAL COMPANY

MIDLAND MICHIGAN

DATA SHEET OF PROPERTIES, HEALTH HAZARDS, AND PRECAUTIONS FOR SAFE HANDLING OF MATERIALS

MOLECULAR FORMULA		CHEMICAL NAME
NO_2		Nitrogen Dioxide
MOLECULAR WEIGHT	**INDUSTRIAL HYGIENE STANDARD**	**SYNONYMS**
46.008	5 ppm	

STRUCTURAL FORMULA - OR COMPOSITION

O = N = O

PHYSICAL AND CHEMICAL PROPERTIES

BOILING POINT	EXPLOSIVE LIMITS (% BY VOL. IN AIR)	FLASH POINT	IGNITION TEMP.	MELTING POINT	VAPOR PRESSURE mm Hg 25°C
Decomp. 21.3 °c 760 mmHg.		°F.	°C.	-9.3 °c.	

CORROSIVENESS (To Common Metals)	PHYSICAL STATE	COLOR
Corrosive to metals if wet.	liquid or gas	Yellow liquid Red-brown gas in con

CHEMICAL REACTIVITY	ODOR (Include Concentration in Air)
Reacts with water to form HNO_3	over 100 ppm

STABILITY (To pH Change, Heat, Light)

TOXIC PROPERTIES

TYPE OF CONTACT		CLASSIFICATION OF TOXIC PROPERTIES	
EYE		☐ May cause no response or no more than very slight to slight transitory pain and/or irritation of the eyelids.	☐ May cause some permanent loss of vision (this includes damage to cornea or internal injury which is incompletely healed in one week.)
		☐ May cause sufficient injury to the eye to result in loss of time from work. (This includes damage to the cornea which heals or nearly heals in a week and/or considerable conjunctival irritation with edema.)	☒ Vapor exposure may cause severe pain, lacrymation or serious injury to the eyes.
SKIN		☐ Single prolonged exposure (hours) causes no effect. Several repeated prolonged exposures may or may not cause the development of some slight irritation.	☐ Single short exposure (minutes) may cause considerable irritation and/or single prolonged or frequently repeated short exposures cause a burn and/or may cause systemic injury, even death.
		☐ Single prolonged exposure may cause some reddening of the skin. Repeated prolonged contacts may cause appreciable irritation, possibly a mild burn and/or may cause appreciable systemic injury due to absorption.	☒ An exposure rapidly causes severe burns ~~and/or serious systemic injury, even death.~~
INHALATION	DUST OR MIST	☐ No systemic injury expected. No irritation to nose and throat in dusty or misty atmospheres.	☐ Dusty or misty atmosphere painful to nose and throat (intolerable to most people) and/or exposure may cause serious systemic injury.
		☐ Throat and nose irritation in a dusty or misty atmosphere is painful but not intolerable and/or prolonged or repeated exposures may cause systemic injury.	☐ Short exposure (minutes) may cause death or serious systemic injury.
	VAPOR	☐ Exposures do not cause any effects other than some very slight irritation or pain to the eyes or respiratory passages at the most.	☐ Exposures may cause extreme drowsiness, and/or serious systemic injury, and/or may cause intolerable irritation to the respiratory passages.
		☐ Single exposures exceeding 1/2 hour, or frequently repeated exposures of shorter duration, may cause slight anesthesia and/or slight systemic injury, and/or cause appreciable, but not intolerable, irritation of respiratory passages.	☒ Short exposures may cause ~~unconsciousness, and/or~~ serious systemic injury, including death.
		☐ Even very short exposure will cause serious systemic injury or death.	
INGESTION		☒ Amounts which may be swallowed incidental to industrial handling will not cause injury. However, if substantial quantities should be swallowed, more or less serious effects may occur.	☐ Amounts which may be swallowed incidental to industrial handling and use may cause serious injury.

COMMENTS

Odor and eye irritation vary little in intensity up to 100 ppm. Persons must leave the area at once if the characteristic brown color of the vapor is evident.

	DEGREES OF EXPOSURE RELATED TO TYPES OF OPERATION	PRECAUTIONS (SEE CODE BELOW)				
		EYES	SKIN	INHALATION* DUST OR MIST	INHALATION* VAPOR	INGESTION
I NO CONTACT	Characterized by remote operation with equipment isolated from the work area. The persons entering isolated areas will require the personal protection outlined for IV below.	A	A		A*	A
II MINOR CONTACT	Characterized by closed systems with equipment vented outside the work area; instrument control; mechanical handling of materials in bulk. Examples are: continuous reactors, stills and filters; enclosed conveyors; ventilated packaging.	C	A		A*	A
III OCCASIONAL DAILY CONTACTS	Characterized by manual handling of materials in packages such as bags, drums and fiberpaks. Ventilation may be provided for specific jobs. Many batch operations fall into this category.	E	D		E	A
IV GROSS CONTACT LIKELY	Characterized by hand operation. Examples are: Emergency repairs, cleaning equipment, cleaning filters, taking care of spills, packaging volatile or dusty materials without ventilation, wheeling and tray drying.	E	E		E	A

EYE CONTACT

- A No eye protection needed.
- B Use safety glasses without side shields.
- C Use safety glasses with side shields.
- D Use chemical workers goggles.
- E Use gas tight goggles or a full face gas mask.

SKIN CONTACT**

- A A bath and clean clothes once per week along with the usual washing at mealtimes should be adequate precautions.
- B Grossly contaminated clothing and shoes must be removed not later than the end of the work period and must be thoroughly cleaned before re-use.
- C Require shower at the end of the work period and clean clothing from the skin out at the start of each work day.
- D Clothing should be changed and skin washed promptly upon any detectable contact. Each use will require special consideration to determine suitable protective devices and standards of personal cleanliness.
- E Impervious clothing such as rubber boots, rubber aprons, and rubber gloves will be required. Specific items will be dictated as required by circumstance.

INHALATION

DUST OR MIST

- A No respiratory protection.
- B No protection required for exposure of thirty min. duration or less to obviously dusty atmospheres. Exposures of longer duration will require the use of a dust respirator bearing the approval of the U. S. Bureau of Mines for the use with toxic dusts.
- D Any exposure to obviously dusty atmospheres will require a dust respirator bearing the approval of the U. S. Bureau of Mines for use with toxic dusts.
- E Any exposure to dusty atmospheres will require the use of an airline respirator, blower mask, or Chemox mask.

VAPOR

- A No precautions necessary.
- B No precautions necessary for single exposures of less than 1/2 hour. Longer single exposures, or frequently repeated exposures will require a gas mask or respirator equipped with appropriate canister.
- C No precautions necessary for single exposures of no more than ten minutes. Longer exposures either single or repeated, will require gas mask or respirator equipped with appropriate canister.
- D Gas mask with appropriate canister required at all times.
- E Evacuate area at once and enter only with airline respirator, blower mask or Chemox mask.

INGESTION

- A No unusual procedures required.
- E Food and tobacco should not be present in the work area. Hands and face should be washed before smoking and eating.

COMMENTS

**GOOD PRACTICE REQUIRES THAT GROSS AMOUNTS OF ANY CHEMICAL BE REMOVED FROM THE SKIN AS SOON AS IS PRACTICAL

*SUITABLE GAS MASK CANISTER

The warning (irritating) properties of nitrogen dioxide are not adequate to prevent acute overexposure.

* Air analyses should be made to check the efficiency of precautionary measures associated with minor contact.

The acid gas and acid gas plus organic vapor canisters do not offer adequate protection. If the chemox or supplied air respirator is used, great care should be taken to avoid entering areas of high concentration (of dense brown fumes as skin irritation will probably result.

SIGNED J. E. Peterson CHECKED D. D. McCollister

DATE 3-13-59 DATE 3-20-59

IV. PROTOTYPE DELIVERY SYSTEM

By

M. F. Katzer

INTRODUCTION

The successful delivery of the formulations that are recommended for application to small hypergolic fires requires specialized equipment. Many of the component parts of such an assemblage were used during the research phase of this contract. The components used during research were very simple and inexpensive because there was no great need for dependability. However, for use in an actual field installation where dependability is essential, the system design must include the very best component parts. Although the system design which is proposed has never been tested, it is believed that standard engineering design criteria can be applied to produce a dependable operational prototype dispersing system. The description of this system is divided into the following sections.

a. GENERAL CONCEPT OR APPROACH

b. HELIPAD LAYOUT

c. MIXING SKIDS

d. AIRBORNE DELIVERY SKID (ADS)

e. OPERATIONAL PROCEDURE

Each section will be discussed and the reasons for many of the recommendations will be explained.

a. GENERAL CONCEPT OR APPROACH

A hypergolic fire of the size being considered will necessarily last only a few minutes. Therefore, it is essential that the extinguishant be transported to the vicinity of the fire in the most rapid manner feasible. It is strongly recommended that consideration be given to the concept of dumping the gelled formulation developed under this contract directly onto the fire from a helicopter. This concept has been developed and widely used by various forestry services for extinguishing forest fires. With practice, the aim of the helicopter pilot can become exceptionally good. For example, a helicopter carrying gelled water was successful in extinguishing a fire high up in a fork of an old redwood tree. All other efforts to extinguish this fire had been unsuccessful. Another example of the exceptional skill that can be developed with a little practice is the case where a charge of water was dropped directly onto a burning automobile to prevent a fire from spreading to an attached house trailer or nearby brush (1). Small helicopters can carry 100 gallons of extinguishant and larger ones have carried as much as 600 gallons. The gellation of the liquid makes it easier to hit the target because the liquid does not break into droplets and is less affected by the wind. Although no work has been done to demonstrate this concept under this contract, the mixing skids that are being proposed could be used to prepare the gelled formulation and pump it directly into the tank of a helicopter.

However, the fire may occur beneath a vehicle or in some location that is completely inaccessible to such an overhead dump. Therefore, for complete control and in order to prevent any rekindling of the fire, it is recommended that an Airborne Delivery Skid be landed as near to the fire as is safely possible. The unit proposed and described in detail under Section D would be delivered via helicopter. The helicopter should be equipped with a double drum winch so that the double cables extending to the unit will have less tendency to twist (see R1-9709). If the cables begin to twist, the suspended unit will gyrate and the pilot will have no directional control of the skid. Ideally, the pilot must maintain directional control so that he can set the unit down in such a position that the third wheel at the front of the unit will point directly toward the fire. This makes it easier to unroll the hose from the hose drum on the unit. Preferably, the hose reel should be mounted on a single-point pivot so that it can turn toward whatever direction the hose is being pulled.

The airborne unit will have wheels rather than skids so that it can be moved by hand, if necessary. A hand brake on the rear wheels will prevent any unintentional movement of the unit. The fire fighting team of three men will be aboard the same helicopter and will debark as soon as the skid is in place. Using the same helicopter for the equipment and men will prevent any possibility of a collision or interference between separate aircraft.

(1) Oakland Tribune, September 10, 1971

While the equipment described is directed toward the problems resulting from an aborted mission, the same equipment and general concepts will apply toward any small fire or potential fire anywhere at the space center. A broken or leaking fuel or oxidizer line anywhere within short range of a helicopter can be dealt with using the same techniques.

b. HELIPAD LAYOUT

The helipad will consist of a concrete pad at least 40' x 30' for the chemical mixing area. The helicopter itself can be parked adjacent to this pad or it can be parked at any conventional airport and flown to the site to pick up the airborne unit.

The helipad will be divided into three areas. One area will be for preparing high viscosity gel. A second area will be for low viscosity gel. The third area is just a parking area for one or more airborne delivery skids.

Each of the preparation areas will have a mixing skid which is described in more detail in Section C. Each area will also have its own prepackaged quantities of chemicals. All of the preweighed components for the preparation of a charge of extinguishant will be stored in separate lockers or compartments so that the operators will know that everything in that compartment must be used. In this way, there can be no inadvertant omission of any of the ingredients.

Table I shows the quantities of the various ingredients which should be prepackaged and stored with one package of each in separate compartments.

TABLE I

PREPACKAGED INGREDIENTS

Additive Number	Chemical Name	Commercial Form and Composition	Weight (Lbs.)	Percentage in Final Product (By Weight)
A.	Material for 150 Gallon Batch of High Viscosity Gel (Total Weight 1,245 Pounds)			
1	Sodium Acetate	100% Powder	102	8.2%
2	Acetic Acid	80% Solution	93	6.0%
3	GELGARD® M	100% Powder	46	3.7%

(Continued on following page.)

(TABLE I continued)

Additive Number	Chemical Name	Commercial Form and Composition	Weight (Lbs.)	Percentage in Final Product (By Weight)
	B. Material for 150 Gallon Batch of Low Viscosity Gel (Total Weight 1,245 pounds)			
1	Sodium Acetate	100% Powder	102	8.2%
2	Acetic Acid	80% Solution	93	6.0%
3	GELGARD® M	100% Powder	37.4	3.0%
	C. Material for 5 Gallons of Standard Buffer Solution for Back Packs (41.5 pounds)			
1	Sodium Acetate	100% Powder	3.4	8.2%
2	Acetic Acid	80% Solution	3.1	6.0%

c. MIXING SKIDS

The design of the mixing skid is shown on the left side of drawing R1-9708. Two of these will be required on the helipad. They are identical except for the Camlock fitting on the end of the delivery hose. These are different sizes in order to prevent the accidental charging of the wrong kind of formulation into the wrong tank on the Airborne Delivery Skid. The component parts of the mixing skid will be described in the order in which they are used during the preparation of the high viscosity extinguishant.

The insulated 200 gallon tank (5A) at the center of the skid is first charged with 125 gallons of water. Refrigerant valves No. 11 should be set to allow refrigerant to circulate through the coils in the two tanks on the skid. The refrigeration system should be started as soon as the water is charged. Valve Number 1 is set to allow recirculation of fluid out of this tank and back into it through line MS-3 to the disperser (2A). Centrifugal Pump #9 is then started. After circulation is started, the pre-weighed powdered additive No. 1 (sodium acetate) is added through the funnel of the disperser. The premeasured amount of liquid additive No. 2 (acetic acid) is then added

directly into the tank. Additional water should be added to bring total volume to 150 gallons. This mixture containing the sodium acetate and acetic acid is referred to as the "Standard Buffer Solution". Continue circulation until the temperature of the standard buffer solution is reduced to about 35°F. At this time, the two way valve #1 is turned so that the chilled fluid begins to transfer through MS-4 and the disperser (2B) into the agitated tank (5B). After 100 gallons of fluid has been transferred, the agitator (3) should be started and the pre-weighed amount of GELGARD® M (additive No. 3) should be charged into the funnel of the disperser (2B). The feed rate of this disperser should be such that the powder is all fed before the remaining 50 gallons of solution has been transferred. After all of the liquid has been transferred, the centrifugal pump can be shut off. Agitation should continue in the second tank until the mass has developed enough viscosity that it cannot experience any segregation. In case there is any concern that the gelled mass is not uniform, valve Number 7 can be set in the recirculation position and gear pump Number 8 can be started. However, such circulation should not be continued for very long or the gel properties may be effected.

After complete gellation (about one hour), the following procedure should be followed to transfer 30 gallons of the contents of the mixing tank to the Airborne Delivery Skid. First, the Camlock fitting (16 or 17) on the end of the hose must be fastened to the proper fitting at the bottom of the tank on the Airborne Delivery Skid. Second, Camlock fittings Number 13 must be connected to the mating fittings on the cooling coils on the Airborne Delivery Skid. Third, both refrigerant valves Number 11 must be turned to permit the refrigerant to flow to the airborne unit as well as through the mixing skid coils. An allowance of about 15 minutes to pre-cool the jacket is desirable. The extinguishant should then be transferred by setting valve Number 7 and starting up gear pump Number 8. The volume transferred will be controlled by the presetting volumetric meter (18). After the proper amount of fluid (30 gallons of high viscosity gel) has been transferred, the pump (8) can be shut down and the transfer hose disconnected and rewound on its reel. The refrigerant system should continue to run to keep the ADS tanks cool until just before the unit is to be picked up by the helicopter.

Exactly the same procedure will be followed in operation of the low viscosity mixing skid except that less GELGARD® M will be added at the time of transfer from one tank to the other. The amount of low viscosity gel to be transferred to the ADS is 50 gallons instead of the 30 gallons. The rest of the operational procedure remains the same.

The procedure calls for the preparation of 150 gallons of each mixture. Only 50 gallons and 30 gallons are transferred. Therefore, there is enough material for three refills. A larger heel of high viscosity gel must remain because its viscosity may cause it to "cone" and bypass air into the gear pump. The larger residual heel prevents this.

COMPONENT PARTS OF MIXING SKIDS

(See Blueprint R1-9708)

(1) 3-Way Valve, (3/4") 2 Ports

(2) Eductor-Dispersers (2 required)

(3) 3 H.P. Electric Agitator Similar to Lightnin Mixer LDG-300 Equipped with 2 Propellers and a Gear Drive to Deliver 100 rpm.

(4) Insulation on Outside of Tank

(5) 200 Gallon Insulated Tank - S.S. (2 reqd)

(6) Base of Skid

(7) 3-Way Valve (1-1/2") 2 Ports

(8) 1-1/2" Gear Pump - Viking - "151" Series
Model No. K-160 - 420 rpm

(9) 50 gpm Centrifugal Pump - 3/4" Piping

(10) Refrigeration Unit

(11) 2-Way Valves to Direct Refrigerant to Airborne Unit

(12) Refrigerant Pump

(13) Refrigerant Lines to Airborne Unit Terminate in Camlock Fittings with Shut-off Valves

(14) Hose Reel

(15) 25 Feet of 1-1/4" Teflon Lined Hose, Type T-4
(S.S. Wire Braid Covering)

(16) 1-1/4" Camlock Fitting with Shut-off Valve for High Viscosity Gel

(17) 3/4" Camlock Fitting with Shut-off Valve for Low Viscosity Gel

(18) 1-1/2" Neptune Industrial Meter Type S-S Auto-Switch Model 432 which automatically shuts off pump (8) when the preset quantity of material has been transferred to the ADS. (Page 17, Catalogue 566-15, Neptune Meter Company)

d. AIRBORNE DELIVERY SKID (ADS)

The Airborne Delivery Skid consists of the two separate tanks for holding the two types of extinguishant formulations. (See drawing R1-9708) Both tanks are 75 gallon (316) stainless steel containers. They are to have hemispherical tops and bottoms and have an operating pressure rating of 300 psi. After pre-cooling for 15 minutes, the tanks are charged with the proper amounts of extinguishant (30 gallons of high viscosity gel and 50 gallons of low viscosity buffer). During this filling operation, the bleed valve at the top of the tank must be open. The floating membrane shown on drawing R1-9708 is an effective means of minimizing "coning" during the discharge operation. In practice, such a membrane has made it possible to eject virtually 100% of the gel from the tanks.

After the tanks are charged with the proper amount of material, valves 5 and 6 are turned from the "fill" position to the "operating" position and a source of high pressure nitrogen gas is connected to both bleed valves 12. The tanks are pressurized to 300 psi. After the 50 gallons of low viscosity gel is ejected, the residual pressure will be 100 psi which is adequate to eject the gel. After the 30 gallons of high viscosity gel is ejected, the residual pressure will be 180 psi which should be adequate to eject this gel through the 100 feet of hose.

Both tanks are connected to a single hose reel on which is wound 100 feet of double or connected hose. One strand of this hose will be 1-1/4" diameter for the high viscosity gel. The other strand will be 3/4" for the low viscosity fluid. Both will be Teflon lined hoses with a S.S. wire braid covering as shown in Catalogue No. G-700 of the Anaconda American Brass Company.

The hoses will terminate in a hand held wand approximately 5 feet in length. The wand is to be 1" diameter thin walled stainless steel or aluminum. Two switches will be built into the handle of this wand so that they can be easily operated with the thumb. Both hands of the operator are available for manipulating the wand. Whichever switch is depressed determines which of the two formulations will flow through the nozzle. The switches control two 12 volt solenoid valves mounted on the two lines just ahead of the hose reel. A 12 volt storage battery on the Airborne Delivery Unit provides the necessary energy to activate the valves. The wand terminates in a 3/4" Vee Jet Nozzle which produces a good spray pattern with these gel formulations.

As mentioned earlier, the Airborne Delivery Skid is equipped with three wheels so that it can be moved by hand if necessary. If the helicopter has placed it just out of reach of the 100' hose, the crew will not be completely helpless. They can release the hand-brake and push the skid closer to the fire. The front wheel is pivoted so it can be used to steer the unit. The lifting hooks are designed in such a way that they will not be in the way of the fire fighters and will not represent a tripping hazard.

COMPONENT PARTS OF AIRBORNE DELIVERY SKID

(See Blueprint R1-9708)

(1) Front Lifting Eye

(2) Rear Lifting Bar

(3) 1-1/4" Camlock for Charging the High Viscosity Gel

(4) 3/4" Camlock for Charging the Low Viscosity Gel

(5) 3-Way Valve 2 Port 1-1/4"

(6) 3-Way Valve 2 Port 3/4"

(7) 1/4" Thick Neoprene Floating Membrane

(8) 8" Diameter Observation and Cleanout Hole

(9) 75 Gallon S.S. Tank

(10) Insulation

(11) Pressure Gauge

(12) Bleed Valve and Pressurization Valve

(13) Camlock Fittings for Refrigerant Lines from the Mixing Skid

(14) 12 Volt Solenoid Valves (3/4" and 1-1/4") Operated by Switches on the Wand

(15) Hose Reel to Hold 100' of 1-1/4 and 3/4" Teflon Lined Hoses (T-4) (Catalogue G-700, Anaconda American Brass Company)

(16) Switches for Operating Solenoid Valves

(17) 5' Wand--1" Diameter Thin Wall Steel or Aluminum

(18) 3/4" Vee Jet Nozzle--50° Angle Cone

(19) 12 Volt Battery for Solenoid Valves

(20) Black, Sivalls and Bryson Safety Head and Rupture Disk

e. OPERATIONAL PROCEDURE

The two hooks that hold the ADS to the lifting cables on the helicopter can be disconnected electrically from the helicopter as soon as the unit is spotted on the ground and the cables slackened. After the ADS has been placed as near to the fire as possible, the 3 man fire fighting crew will debark. One man will unlock the hose reel and then observe the pressure gauges to be sure the system is still completely operational after being picked up and delivered. He will then remain behind as a safety backup man. The other two men will quickly pull the hose and the wand toward the fire. Upon arrival at the scene, they must determine which of several procedures to use.

(1) If both fuel and oxidizer are escaping and a hypergolic fire is burning, the high viscosity gel (3.7% GELGARD® M) will be used to build a dam between the ingredients to try to separate the two sources. This same high viscosity gel can be laid down as a blanket to act as a "sink" for the N_2O_4 to fall onto and be neutralized. The "hydrazine in air" fire that will continue to burn after the hypergolic fire has been stopped can best be extinguished by applying a fog of standard buffer solution. Very little liquid is needed for such a fog system. It is proposed that this be carried in a nitrogen pressurized 5 gallon back pack or hand-carried type of fire extinguisher. Several such prepressurized units can be mounted on the ADS and when needed, the third man of the fire fighting team can bring one forward. These extinguishers should be filled with the same standard buffer solution as was prepared in tank (5A) but before the addition of the GELGARD® M. Prepackaged quantities of the two necessary ingredients are described in Table I.

(2) If only N_2O_4 is escaping and no fuel is apparent, the high viscosity gel can be used to cover the N_2O_4 and can be spread out as a blanket to act as a "sink" for any future spill. This will prevent a hypergolic reaction if a fuel leak develops later. It will also help to neutralize the N_2O_4 and decrease the fuming.

(3) If fuel is escaping but no oxidizer is present yet, the low viscosity buffer solution (3.0% GELGARD® M) should be used to dilute and neutralize the fuel. It would also be prudent to observe where the oxidizer might come from if a leak develops. The high viscosity gel (3.7% GELGARD® M) should then be placed as a blanket so that in the event of such a leak, the oxidizer would be quickly neutralized by the buffer ingredients. In addition to the blanket, a dam could be constructed with the 3.7% gel in order to prevent intermixing in case the second ingredient starts to leak. This will minimize the possibility of a hypergolic reaction from occurring.

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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